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(Summary Report)

STABLE WHITE COATINGS

September 21, 1961, to July 15, 1963

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(Subcontract under NASA Contract NAS7-100)
IITRI Project C207

This report was prepared by the IIT Research Institute, Chicago, Illinois, under the direction of the IITRI Project C207, which is a subcontract under NASA Contract NAS7-100.

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FOREWORD

This is Report No. IITRI-C207-25 (Summary Report) of Project C207, Contract No. 950111 (subcontract under NASA Contract NAS7-100), entitled "Stable White Coatings." The report covers the period from September 21, 1961 to July 15, 1963. Previous Interim Reports, No. ARF-3207-5 and ARF-3207-14, were issued in April 1962 and November 1962, respectively. This report is prepared for Mr. William F. Carroll, JPL Cognizant Engineer.

Major contributors to the program included Gene A. Zerlaut (Project Leader); Y. Harada and Harold L. Rechter (inorganic coatings); Richard J. Larson (space-chamber operation); O. Harry Olson (optical measurements); Dr. Caroline D. Miller (ultraviolet effects and general consultation); Dr. N. E. Boyer, William Sumida, and John Brzuskiwicz (organic preparations); Edwin H. Tompkins (zinc oxide photolysis studies and general consultation); William L. Stepp (silicone synthesis); and Douglas G. Vance (methyl silicone synthesis and silicone paint preparations). Contributions to this report were made by O. H. Olson, C. D. Miller, E. H. Tompkins, R. J. Larson, and H. L. Rechter.

Data are recorded in Logbooks C9164, C11712, C11934, C12115, C12238, C12283, C12750, C13031, C13046, C12683, C13084, and C13408.

Respectfully submitted,

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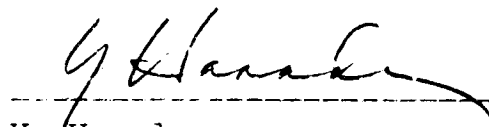
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ABSTRACT

STABLE WHITE COATINGS

Investigations were conducted to develop a white thermal-control coating for spacecraft. The primary requirements were that the paint possess good stability to ultraviolet irradiation in vacuum, that the maximum allowable change in the ratio of solar absorptance to emittance be only 10% after one year of extraterrestrial solar radiation, that the ratio of solar absorptance to emittance be 0.20 ± 0.05 , and that the emittance be approximately 0.90. The other requirements were that the coating cure at less than 300°F and that it adhere to materials such as aluminum and conversion-coated magnesium through temperature changes of 50°F per minute between 200 and -100°F.

Of the pigments studied, zinc oxide, zinc sulfide, and calcined china clay were the most satisfactory, in that order. Of the vehicles, methyl silicones and alkali silicates were the most satisfactory. After zinc oxide was selected as the pigment, developmental work concerning formulation and application was conducted to determine the best combination of physical and optical properties for both organic and inorganic coatings. The desired properties were obtained through the use of a high-purity zinc oxide, SP 500, in conjunction with either a methyl silicone polymer synthesized in our laboratories or a commercial potassium silicate, PS7. Both systems changed less than 0.02 in solar absorptance after an exposure of over 4000 equivalent sun-hours.

It is concluded that satisfactory passive thermal control can be achieved with coatings of methyl silicone-bonded or potassium silicate-bonded zinc oxide. The paint must be stringently clean in order to prevent photolysis of contaminants, such as sebum and organic solvent residues.

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GLOSSARY

| | |
|---------------------------|---|
| α | Solar absorptance. |
| α_1 and α_2 | $\alpha_1 + \alpha_2 = \alpha$. α_1 corresponds to that half of the sun's energy below 700 m μ , and α_2 corresponds to that half above 700 m μ . |
| $\Delta\alpha$ | Change in absorptance. |
| ϵ | Emittance. |
| α/ϵ | Ratio of solar absorptance to infrared emittance. |
| ESH | Equivalent sun-hours. |
| Me/Si | Molar ratio of methyl groups to silicon atoms. |
| PBR | Pigment/binder ratio. |
| PVC | Pigment volume concentration. |

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STABLE WHITE COATINGS

I. INTRODUCTION

The principal objective of this program was the development of a white spacecraft-thermal-control coating with exceptional stability to extraterrestrial solar radiation. Therefore the primary requirements were that:

- the coating have a high resistance to ultraviolet radiation in vacuum, namely, the change in the ratio of solar absorptance to infrared emittance be only 10% after 1 year of exposure
- the ratio of solar absorptance to infrared emittance of the coating be 0.30 or less
- the infrared emittance of the coating be approximately 0.9.

The other requirements were that:

- the coating cure at 300°F or less
- the coating remain adherent to aluminum alloys and other spacecraft structural materials through temperature changes of 50°F per minute between 200 and -100°F.

Emphasis was directed more to the change in value than to the absolute value of solar absorptance. Accordingly, the measurement of spectral reflectance within the solar region was directed more toward precision than toward absolute accuracy.

Pigmented coatings, i.e., paints, were studied rather than evaporated metal films or chemical conversion coatings because of practical considerations. First, the ease of application of paints permits the employment of thermal-control coatings at convenient times during the fabrication of spacecraft. Second, painted surfaces are more easily recoated in the event of thermal-design changes or the occurrence of soiled and damaged areas.

Conventional or commercial coatings were not studied because they deteriorate rapidly under ultraviolet irradiation in vacuum. Instead, experimental laboratory formulations with known ingredients, purities, and weight ratios were investigated. Since very few materials have the stability required for long-range space probes, some unusual formulations were studied. The work was divided broadly into organic and

inorganic coatings. Organics tend to provide better adhesion and certain other mechanical properties whereas inorganics tend to possess better ultraviolet stability. The established adhesiveness, low curing temperature, absence of color, and refractoriness of the alkali silicates made them a logical choice for evaluation as paint vehicles.

In order to reduce the complexity of the problems involved, pigments and paint vehicles were exposed individually to ultraviolet radiation in vacuum. These screening experiments were the basis for the subsequent choice of potentially stable paint formulations. Determination of spectral reflectance and solar absorptance before and after exposure showed that no material studied was completely unaffected by ultraviolet irradiation in vacuum -- a result which is consistent with the findings of other workers. Zinc oxide and, to a lesser extent, zinc sulfide were found to be unusually stable white pigments and formed relatively stable coatings when dispersed in pure potassium silicate or in methyl silicone polymers.

The bulk of the research effort was devoted to the development of still more stable pigmented potassium silicate and methyl silicone paints. Various methyl silicone resins were synthesized in attempts to improve both their ultraviolet stability and their film-forming characteristics. The physical and optical properties of the silicate and silicone paints were measured as functions of paint thickness and composition. The effects of soiling and cleaning candidate coatings were studied in an attempt to define the problems anticipated during spacecraft fabrication and during checkout just prior to launch. Dirt-impervious or cleanable coatings of intermediate low solar absorptance are preferable in practice to noncleanable coatings of exceptionally low solar absorptance when permissible from the standpoint of thermal design.

Many interesting observations were not investigated because of lack of time and resources. These observations, together with descriptions of several special investigations which were not followed to conclusion, are discussed in the section on related investigations, Section X.

The requirement for high stability to the space environment includes not only the solar ultraviolet as a consequence of the sun's temperature but also other radiations in space, primarily galactic (cosmic) proton radiation and trapped charged particles in the Van Allen belt. Adequate simulation of solar ultraviolet below 2000 Å including Lyman alpha as well as the high-energy particulate radiations, is both difficult and expensive. Furthermore, of a total of 135 watts per square foot at earth-distance, less than 0.25 watts per square foot of electromagnetic radiation is radiated below

2000 A, whereas about 12 watts per square foot is radiated between 2000 and 4000 A in the near-ultraviolet. Since the development of stability to high-energy radiations is useless unless stability to the more prevalent near-ultraviolet is assured, space-simulation efforts were confined to the near-ultraviolet region from 2000 to 4000 A at a vacuum in the range of 10^{-7} torr.

The establishment of the exceptional stability of zinc oxide and the development of semiorganic methyl silicone polymers with stabilities comparable to those of the alkali silicates emerge as the most rewarding aspects of the program.

II. OPTICAL MEASUREMENTS

A. Solar Absorptance

Solar absorptance was determined indirectly by measurement of spectral reflectance in the wavelength range of 0.3 to 2.7 μ (300 to 2700 $m\mu$). The reflectance data were integrated with solar spectral energy data¹ for the upper atmosphere to yield solar reflectance. Subtraction of the solar reflectance from unity yielded solar absorptance. Comparison of these solar spectral energy data with the data of Nicolet² showed that solar absorptance agreed within 0.005.

A General Electric recording spectrophotometer, which employs approximately normal illumination and diffuse viewing of a sample surface, was used for the visible spectrum, 380 to 700 $m\mu$; and an integrating-sphere reflectometer of our own design was used for both the ultraviolet and infrared regions. The latter incorporates a Perkin-Elmer quartz monochromator as a dispersing system along with appropriate sources and detectors. Figure 1 is a schematic diagram of the optical arrangement of the infrared reflectometer. For the infrared region, a ribbon-filament incandescent lamp was a satisfactory source and the detector was a lead sulfide photoconductive cell. For the ultraviolet region, a mercury arc or hydrogen lamp was used as the source with a photo-multiplier detector.

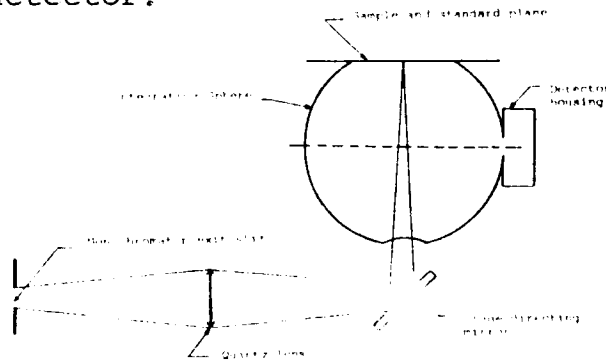


Figure 1

INTEGRATING-SPHERE REFLECTOMETER

¹"Smithsonian Physical Tables" 9th ed

²Nicolet, M., Chap. XII in "Solar Physics and the Atmosphere of the Earth," C. S. White and O. O. Benson, Jr., ed., Univ. New Mexico Press, Albuquerque, 1952.

Both reflectometers measure reflectance relative to a standard. These are comparison instruments, since the sample and the standard are both in place at all times. Magnesium oxide was used as the standard, and the relative reflectance data obtained were converted to the absolute basis by using the absolute reflectance data of magnesium oxide published by Middleton.^{3,4} Reflectance data which are presented in the tables are limited to values at 440- and 600-m μ wavelength.

Since it was not economical to provide solar absorptance values during the extensive screening operations, for many materials the effect of space simulation was evaluated in terms of reflectance losses in the visible region. This method is considered satisfactory, since the predominant losses occur in the 400- to 600-m μ wavelength region for most white and transparent materials.

In many cases solar absorptance values are reported as a_1 and a_2 , where

$$a = a_1 + a_2$$

a_1 corresponds to that half of the sun's energy spectrum which lies below 700-m μ wavelength, and a_2 corresponds to that half which lies above 700 m μ . By splitting a into two components, that region of the spectrum undergoing the most significant change in absorptance is more readily described. For example, some formulations show little change in solar absorptance on irradiation, but their reflectance decreases in the visible region (increase in a_1) and is counterbalanced by a corresponding increase at longer wavelengths (decrease in a_2).

B. Total Normal Emittance

Total normal emittance was measured with the equipment shown in Figure 2. Test samples and a calibrated standard were mounted vertically in a sample tray and heated in a horizontal tubular furnace. The sample tray was given a slow reciprocating motion parallel to the axis of the furnace by a mechanism not shown in the diagram. The total sample travel was about 14 inches, which permitted five samples in the tray to pass a viewing port, to be viewed by a suitable detector, twice per cycle. The specimens were viewed through a

³Middleton, W. E. K., Journal of the Optical Society of America, Vol. 41, No. 6, 1951

⁴Middleton, W. E. K., Journal of the Optical Society of America, Vol. 43, No. 1, 1953.

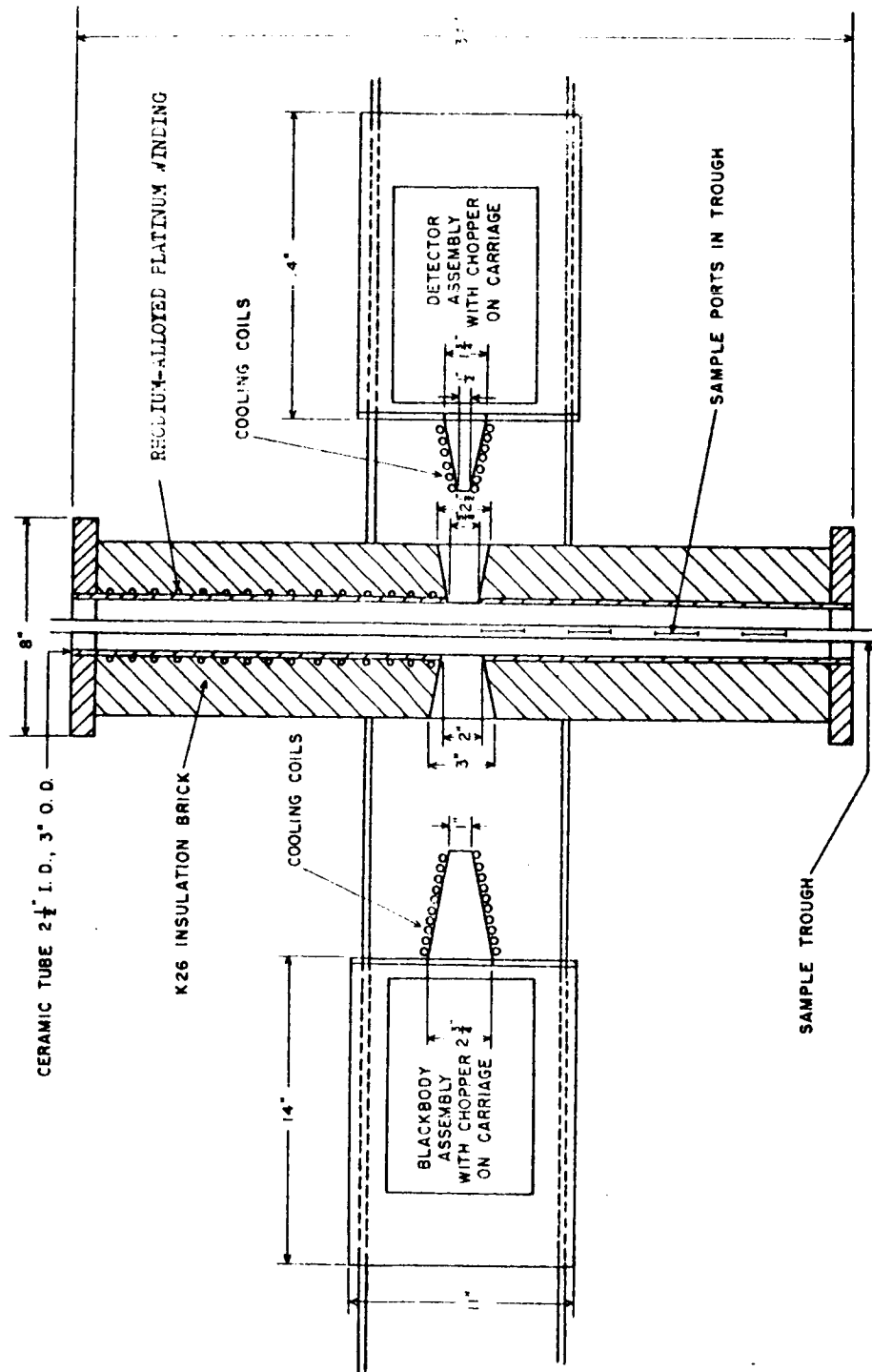


Figure 2
APPARATUS FOR MEASURING EMITTANCE

water-cooled cone, which was introduced with its nose close to the test surface at the time measurements were being made. The cone served as a radiation shield and prevented radiant energy originating in the furnace walls from falling on the test surface and subsequently being reflected to the detector. Since the samples and the standard were heated in the same furnace, this method avoided the dangers of temperature errors associated with separately heated samples and standards.

Comparison of signals from the samples and the calibrated standard yielded the desired emittance values. The standards used were Pyroceram 9606 and polycrystalline silicon carbide, and they were calibrated against a carefully designed blackbody cavity.

The method does not lend itself to emittance determinations at room temperature, since the temperature of the specimen being tested must be raised above that of the detector in order to obtain a working signal. This is not a serious limitation, however, since total emittance, in general, is a mild function of temperature. Total emittances determined at approximately 200°F, which is adequate with the equipment described, closely approximate room-temperature values. This program was concerned more with determination of any effects of space simulation upon the coatings than with determination of the absolute emittance values per se.

III. SPACE SIMULATION

A. Vacuum Simulation

1. Oil-Diffusion Pump

The vacuum of the space environment is variously quoted at 10^{-9} to 10^{-15} torr, but the attainment of such pressures in the laboratory is time-consuming and probably unnecessary for the purposes of this work. At much higher pressures, 10^{-6} torr, there is no evidence of oxidative degradation. Also, the mean free path of evolved molecules is large compared to the dimensions of the chamber, so that further reduction in pressure would not be expected to change the results of space-simulation tests. The problem of oxygen exclusion is discussed in Section IX.

These principles guided the design of the space-simulation chamber shown in Figure 3 which was used in the early screening operations. It consists of a cylindrical chamber 24 inches in diameter and 24 inches high, cooled by refrigerant coils on its outer surface and capped with a torispherical head in which three General Electric mercury-arc AH-6 lamps are mounted. The distance from the lamps to the samples, which are mounted on a turntable beneath the lamps, can be adjusted to achieve variation of radiation intensity. The radiation intensity varies at different distances from the center of the turntable, so various acceleration factors are possible. The constancy of the radiation is monitored by reflecting a portion from a first-surface mirror, mounted over the center of the turntable, through a quartz window on the head. The absolute intensity is measured before and after each run by using a wide-angle, temperature-compensated thermopile.

Several types of sample turntables are available. The simplest is a 16-inch flat plate, suitable for use when no measurements are to be made in the chamber. Typically, this was used when the reflectivity of a number of materials was to be measured before and after irradiation. The turntable assures that all samples receive equivalent exposures at a given radial distance. It is rotated by a 12-point Geneva drive and a 2-rpm fractional horsepower motor in a welded housing which is open to the atmosphere through ventpipes in order to eliminate the problems associated with operating motors in a vacuum.

The chamber is mounted on a 10-inch oil-diffusion pump, National Research Corporation model H-10-SP, with an approximate pumping speed of 4000 cfm at 10^{-4} torr. In practice, the pump reaches 10^{-6} torr routinely, and all ultraviolet testing was performed at this level or below. However, it became desirable

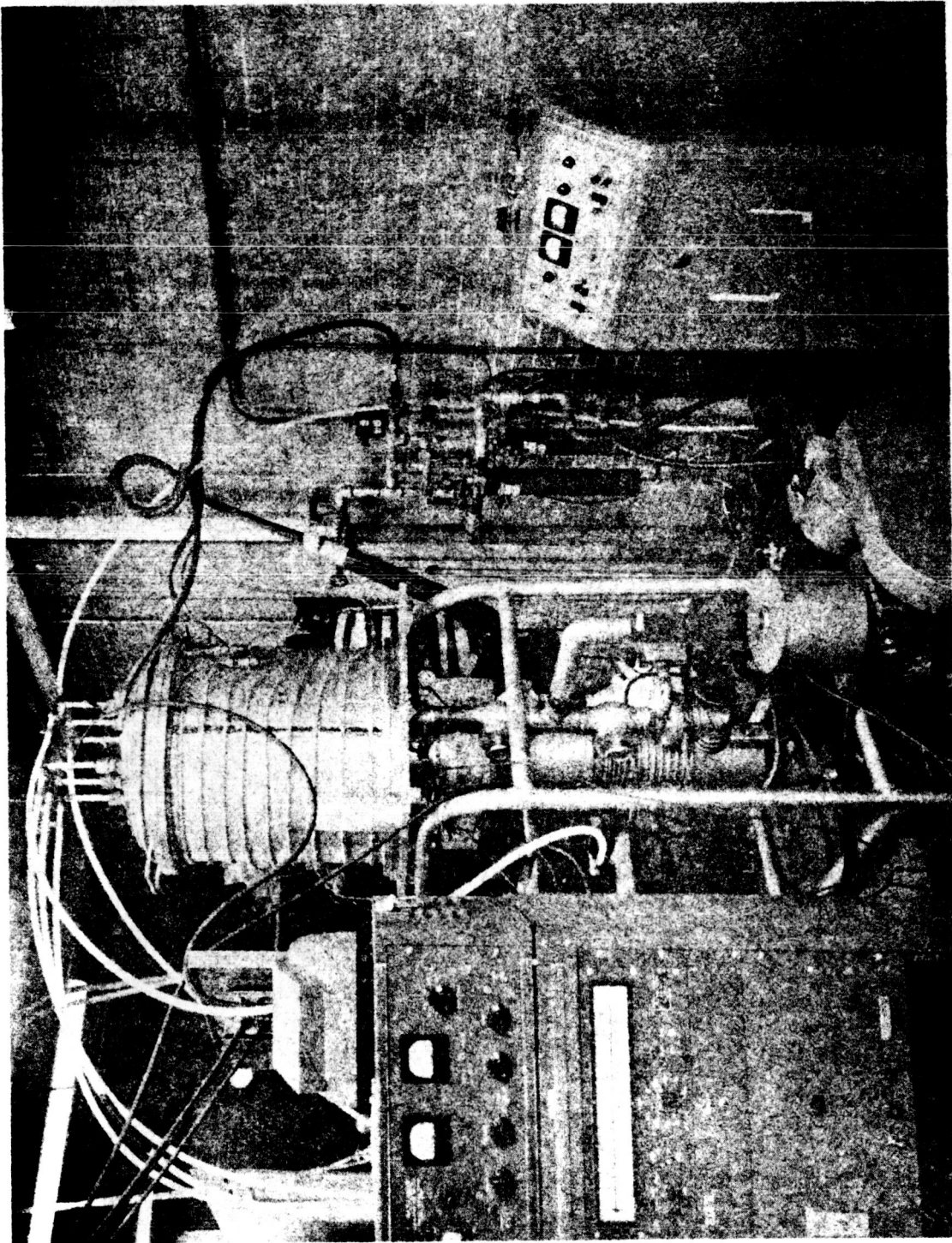


Figure 3
DIFFUSION-PUMPED SPACE-SIMULATION CHAMBER AND ASSOCIATED EQUIPMENT

to sacrifice both pumping speed and ultimate vacuum in favor of more efficient trapping of pump oil. In some of the early experiments backstreaming was very high; oil condensed on the cold-water jackets and photolyzed to a highly absorbent varnish which attenuated much of the ultraviolet radiation from the lamps. Deposition of varnish was greatly reduced by employing a trap filled with a molecular sieve (Linde 13x) in series with an optical trap refrigerated with liquid nitrogen.

The samples were of many forms: pigmented and clear films, free and on a substrate, compacted and loose powders. For uncooled samples, as used in this equipment, the nominal specimen temperatures were 150°F at an intensity of about 3 solar equivalents.

A second chamber was constructed for the oil-diffusion-pumping station. It is a cylindrical chamber 24 inches in diameter and employs a flat head with a quartz window mounted in the center. The AH-6 lamp is mounted externally to the chamber in order to eliminate formation of varnish on the lamp water-jacket. The samples are mounted on a water-cooled table which can be adjusted in height. The table is mapped for different lamp-to-table distances, and absolute intensity is measured by a wide-angle thermopile.

Pertinent data for the two chambers are presented in Table 1. The Geneva-drive chamber was used for general screening tests A through F, and the chamber with the externally mounted lamp was used for tests AA and BB.

Table 1

PERTINENT DATA ON SPACE-SIMULATION TESTS
EMPLOYING THE OIL-DIFFUSION PUMP

| Test | Avg. Solar Factor | Time hr | Exposure ESH | Operating Pressure, torrs | |
|------|-------------------------|------------|-----------------|------------------------------|----------------------|
| | | | | Initial | Terminal |
| A | 1.5 | 50 | 75 | 1×10^{-5} | 2.5×10^{-6} |
| B | 4 | 17 | 68 | 1×10^{-5} | 1×10^{-5} |
| C | 3 | 60 | 180 | 1×10^{-5} | 9×10^{-6} |
| D | 3 | 67 | 200 | 9×10^{-6} | 1×10^{-6} |
| E | 3 | 100 | 300 | 1×10^{-5} | 2×10^{-6} |
| F | 2.5-3 | 90 | 225-270 | 7×10^{-6} | 1.5×10^{-6} |
| AA | 7-9 | 69 | 485-630 | 5×10^{-6} | 4.5×10^{-7} |
| BB | 8-11 | 138 | 1140-1580 | 1×10^{-6} | 3.5×10^{-7} |

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2. Ion Pump

An ion-pumped space-simulation chamber was constructed and was used for longer-term tests. The system provides a convenient means of obtaining a clean ultrahigh vacuum. The chamber dimensions are given in Figure 4. The chamber is provided with a quartz window and a liquid-cooled sample table. The table, shown in Figure 5, can be cooled with liquid nitrogen, ice water, or tap water and can accommodate six 1- x 1-inch specimens. The system, shown in Figure 6, consists of a 400-liters/sec Varian VacIon pump, which is prepumped with both a molecular-sieve sorption pump and a mechanical pump. An AH-6 lamp is mounted over the quartz window, which is shown in place in Figure 6. Reproducible equivalent solar factors, as determined with a temperature-compensated thermopile, were achieved from 4 to 18 intensities (2000 to 4000 A). A plot of $1/D^2$ (D = distance from the lamp to the sample table) resulted in a straight-line relation.

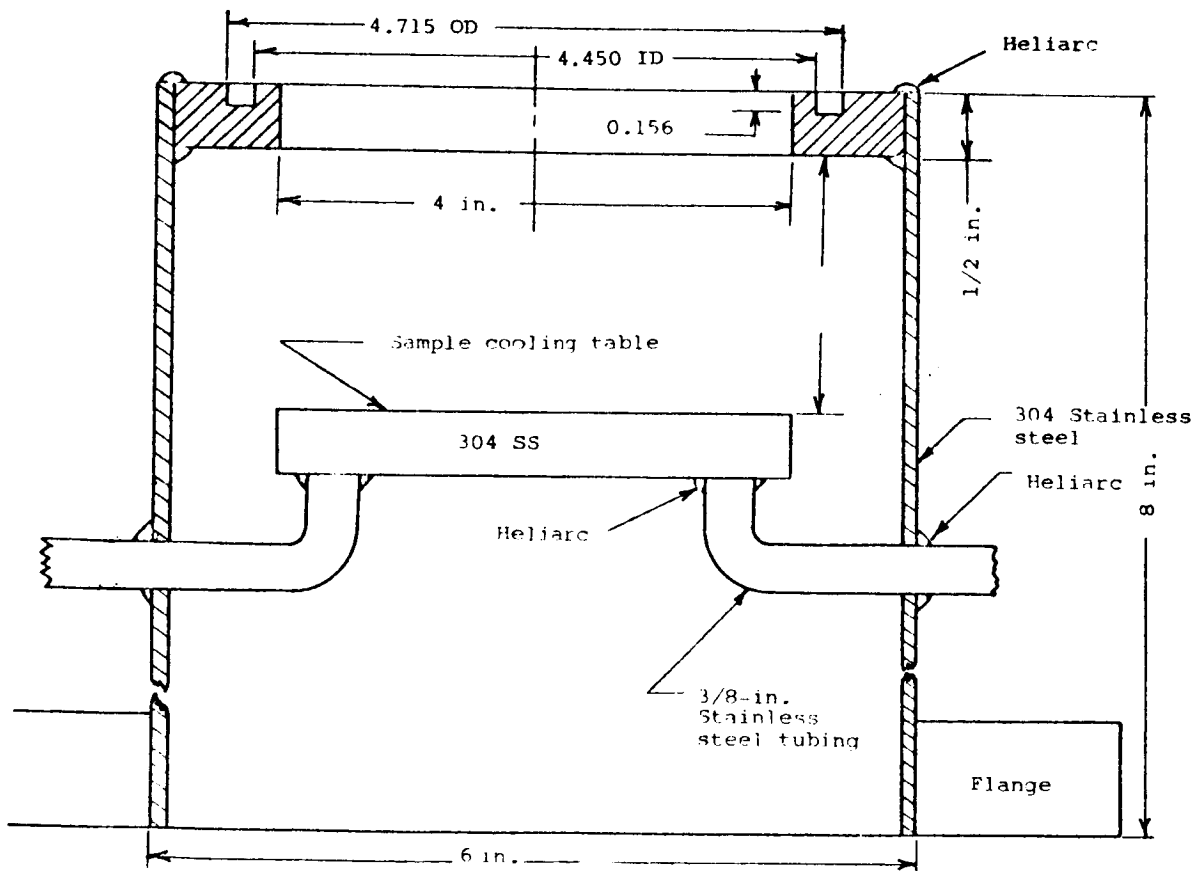


Figure 4

DIAGRAM OF ION-PUMPED SPACE-SIMULATION CHAMBER
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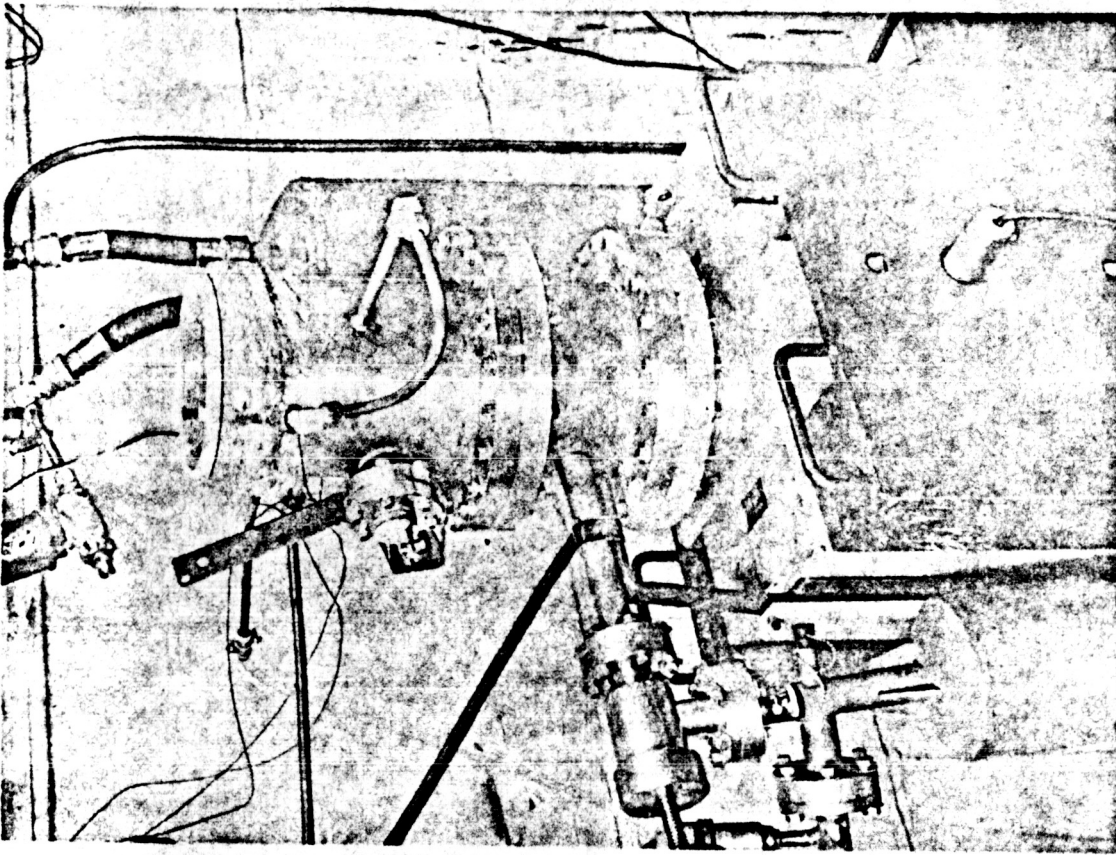


Figure 6
ION-PUMPED SPACE-SIMULATION CHAMBER

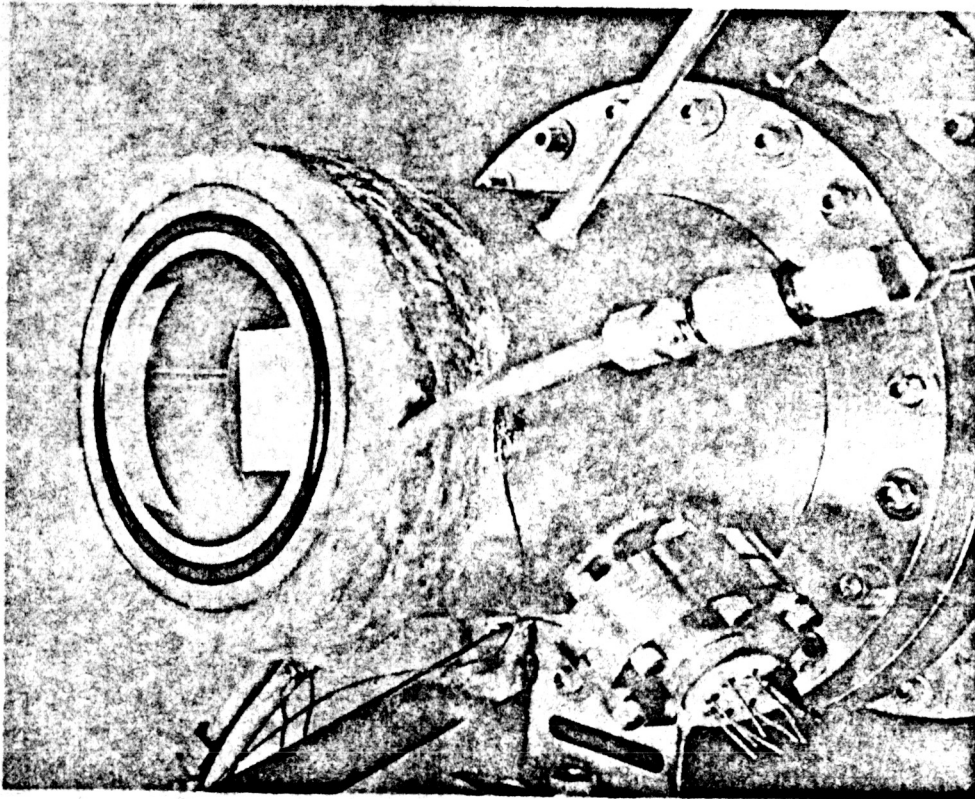


Figure 5
ION-PUMPED SPACE-SIMULATION CHAMBER
WITH SAMPLES IN PLACE

Pertinent data for the ion-pumped space-simulation tests are presented in Table 2.

Table 2

PERTINENT DATA ON SPACE-SIMULATION TESTS
EMPLOYING THE ION PUMP

| Test | Avg. Solar Factor | Time, hr | Exposure, ESH | Operating Pressure, torrs | |
|------|-------------------------|-------------|------------------|------------------------------|--------------------|
| | | | | Initial | Terminal |
| 1 | 10 | 45 | 450 | 3×10^{-7} | 1×10^{-8} |
| 2 | 10 | 210 | 2100 | 5×10^{-7} | 3×10^{-8} |
| 3 | 8.7 | 195 | 1700 | 5×10^{-7} | 2×10^{-8} |
| 4 | 10 | 120 | 1200 | 5×10^{-7} | 4×10^{-8} |
| 5 | 10 | 313 | 3100 | 5×10^{-7} | 2×10^{-8} |
| 6 | 9 | 162 | 1460 | 3×10^{-7} | 2×10^{-8} |
| 7 | 17.6 | 191 | 3350 | 5×10^{-7} | 5×10^{-8} |
| 8 | Test failed | | | | |
| 9 | 10.7 | 158 | 1700 | 5×10^{-7} | 3×10^{-8} |
| 10 | 21 | 25 | 525 | 2×10^{-6} | 6×10^{-7} |
| 11 | 11 | 144 | 1600 | 5×10^{-7} | 1×10^{-7} |
| 12 | 13.6 | 41 | 555 | 2×10^{-6} | 3×10^{-7} |
| 13 | 10.7 | 297 | 3180 | 1×10^{-6} | 3×10^{-8} |
| 14 | 17.9 | 185 | 3300 | 3×10^{-7} | 6×10^{-8} |
| 15 | 9 | 185 | 1670 | 5×10^{-7} | 7×10^{-9} |
| 16 | 10.1 | 183 | 1850 | 8×10^{-7} | 1×10^{-8} |
| 17 | 10.2 | 168 | 1720 | 8×10^{-7} | 5×10^{-9} |
| 18 | 10.2 | 156 | 1600 | | 3×10^{-8} |
| 19 | 11.1 | 90 | 1000 | 8×10^{-7} | 5×10^{-8} |
| 20 | 5.4 | 185 | 1000 | 1×10^{-6} | 3×10^{-8} |
| 21 | 9.5 | 189 | 1780 | 2×10^{-7} | |
| 22 | 9 | 184 | 1650 | 3×10^{-6} | 5×10^{-8} |
| 23 | 10.6 | 392 | 4170 | 5×10^{-7} | 4×10^{-8} |

B. Solar Simulation

1. AH-6 Lamp

The solar spectrum is given in Figure 7. Also shown in Figure 7 is the energy spectrum of a typical AH-6 lamp at comparable total intensity. The wavelengths below 2000 Å contribute less than 0.1% of the total energy and so can be disregarded without significant error. Wavelengths above 4000 Å can be disregarded because they are not sufficiently energetic to break bonds, although approximately 90% of the energy is found at these longer wavelengths and the total suitability of a coating for passive temperature control depends to a great degree upon its reflectance in the visible region of the spectrum. On the basis of these considerations, the General Electric AH-6 lamp, a quartz-jacketed water-cooled high-pressure mercury arc, was selected as the source for ultraviolet radiation.

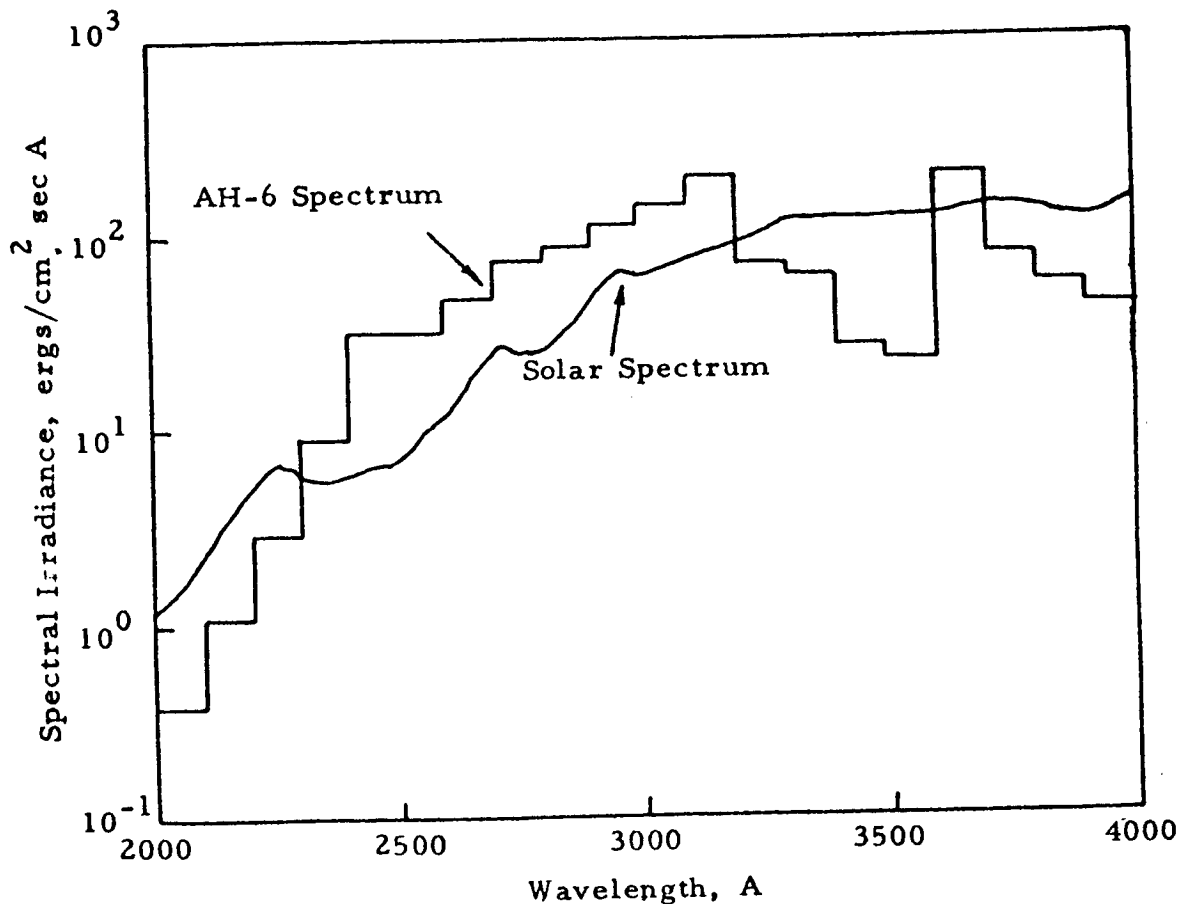


Figure 7

COMPARISON OF THE SOLAR SPECTRUM
WITH THE SPECTRUM OF AN AH-6 LAMP
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2. Measurement of Lamp Intensity and Solar Factor

The total lamp intensity was measured with a wide-angle, temperature-compensated thermopile obtained from the Eppley Laboratories, Inc. The thermopile, shown in Figure 8, has a constant of 6.98 millivolts/cal/cm²/min. From the thermopile output, the solar factor was calculated as follows.

$$\frac{\text{thermopile output (millivolts)}}{2 \times \text{thermopile constant}} = \text{cal/cm}^2/\text{min}$$

The thermopile output was divided by 2, since half of the total energy of the lamp is assumed to be below 4000 Å. The solar intensity at wavelengths below 4000 Å has been determined to be 13 milliwatts/cm². Cal/cm²/min was converted to milliwatts/cm² by applying several conversion factors. By dividing this value by "one" solar factor of 13 milliwatts/cm², the number of "suns," or the equivalent solar factor, for a given thermopile output was obtained. Solar factors were determined for various lamp-to-sample distances in the ion-pumped chamber:

| <u>Solar Factor</u> | <u>Distance from Lamp to Sample, inches</u> |
|---------------------|---|
| 5.2 | 9.00 |
| 6.1 | 6.40 |
| 10.3 | 5.40 |
| 12.2 | 4.75 |
| 13.2 | 4.33 |
| 15.9 | 4.00 |

The AH-6 lamp is positioned over the samples at a distance corresponding to the solar factor desired. A small recording thermopile is positioned over the lamp and is used to monitor changes in the lamp intensity over periods of time. This information is valuable in assigning an equivalent sun-hour radiation value to a given space-simulation experiment.

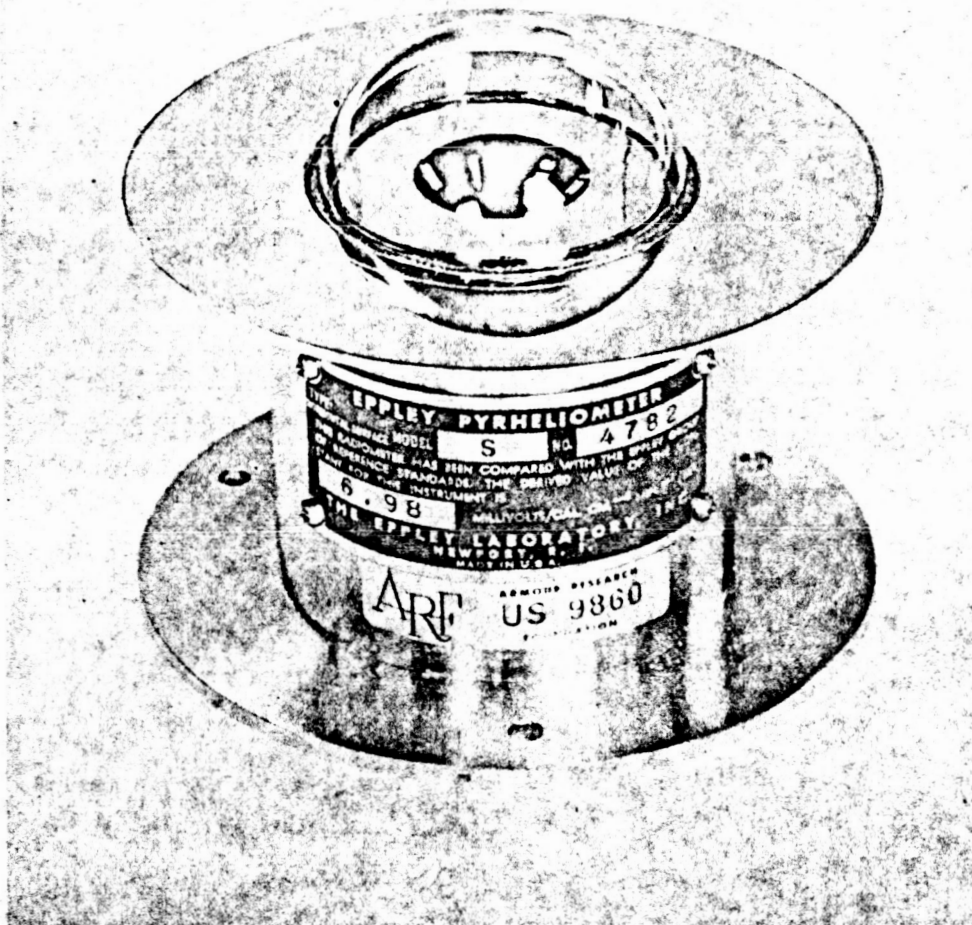


Figure 8

WIDE-ANGLE THERMOPILE
FOR MEASURING EQUIVALENT SOLAR-ULTRAVIOLET FACTOR

3. Lamp Degradation

Assessment of the damage caused by space-simulation tests could be in error if the spectral output of the ultraviolet source were reduced disproportionately, i.e., if the radiation below about 2800 Å decreased with lamp age at a higher rate than the longer-wavelength ultraviolet. Therefore, attempts were made to measure the spectral output of several AH-6 lamps before and after operation. A Seya-Namioka vacuum-ultraviolet monochromator manufactured by Jarrell-Ash was used.

The results were inconclusive. There appeared to be a disproportionate decrease in peak intensity at 2285 and 2535 Å. The decrease, if interpreted properly, amounted to 20%. No such trend was discerned for the lower-wavelength continuum. It was therefore concluded that calculations of exposure (equivalent sun-hours) on the basis of the overall drop in lamp intensity during a given test were reasonably accurate and meaningful.

The criteria for changing lamps were either a 30% decrease in the overall lamp intensity, as measured with the recording thermopile, or the incipient erratic behavior of a lamp, whichever occurred first. By these criteria the average lifetime was 80 to 100 hours of continuous operation. Some lamps maintained constant behavior at above 70% of their initial intensity for as long as 200 hours. Others began to flicker within two or three hours and had to be replaced.

4. Transmission Losses Due to Varnish Formation

In some of the early experiments with the oil-diffusion-pumped system, backstreaming was very high. The backstreamed oil that condensed on the cold-water jackets of the internally mounted AH-6 lamps photolyzed to an ultraviolet-absorbing varnish which reduced the total radiation by 20% in 50 hours. Most of the loss was concentrated in the important, short wavelengths. Typical data for spectral output of the lamps before and after deposition of this varnish are shown in Figure 9. The bulk of this loss in output was eliminated by the use of a chamber with externally mounted lamps.

Varnish also formed on the quartz window in the ion-pumped space-simulation chamber. The varnish was removed after each test by heating the window in boiling chromic acid. The effect of varnish upon the transmittance of the quartz window is presented in Figure 10. The upper curve shows the transmittance of a clean window, and the bottom curve shows the transmittance after several of the early tests in which the ion pump was first used. The middle curve is the transmittance after one run only. In the final procedure adopted, the transmittance of the quartz window was measured in each test both before and after cleaning. No permanent effect due to irradiation was noted.

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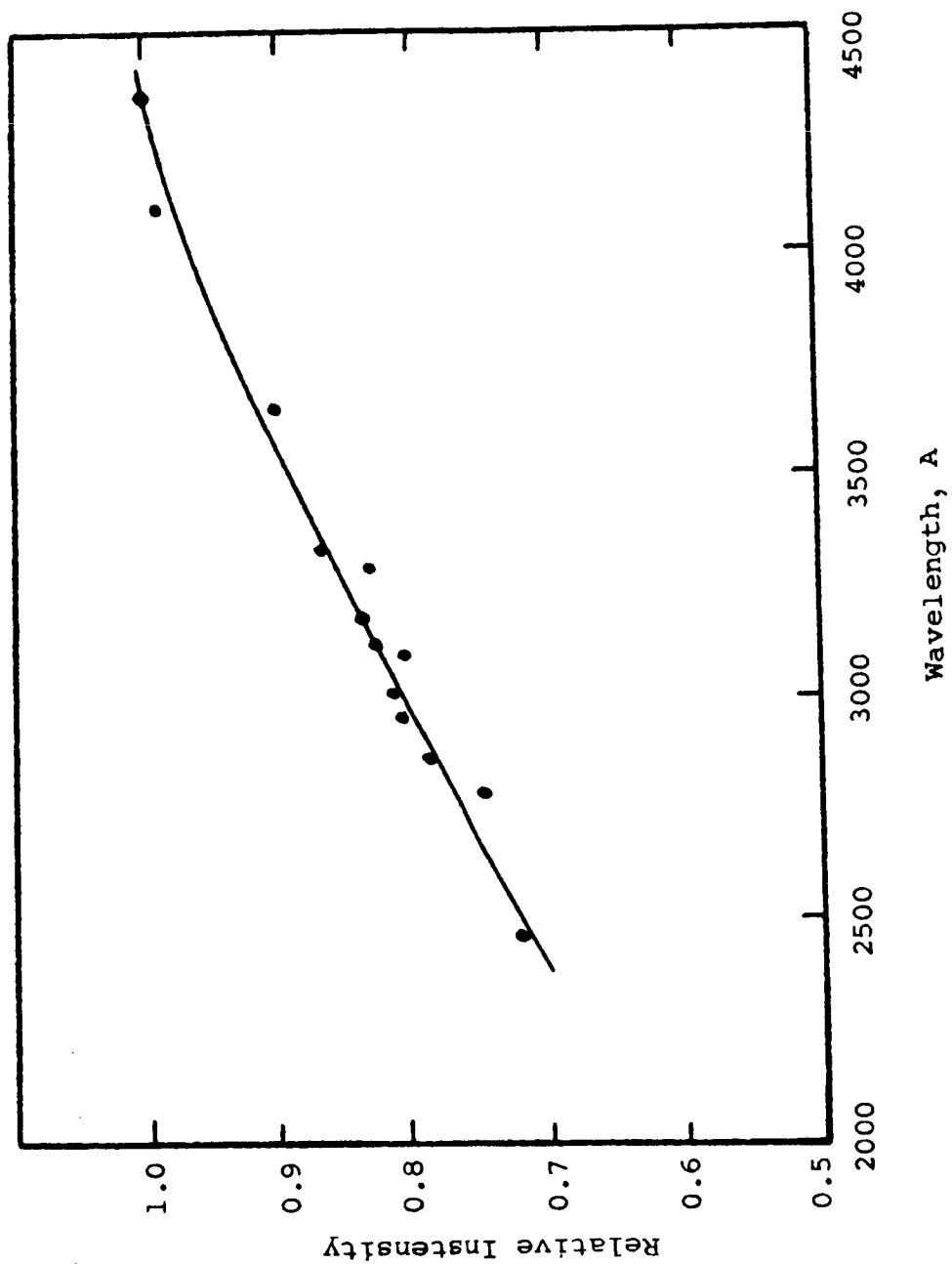


Figure 9
TRANSMITTANCE LOSSES DUE TO VARNISH FORMATION
AND LAMP DEGRADATION IN AH-6 LAMPS USED FOR 50 HOURS

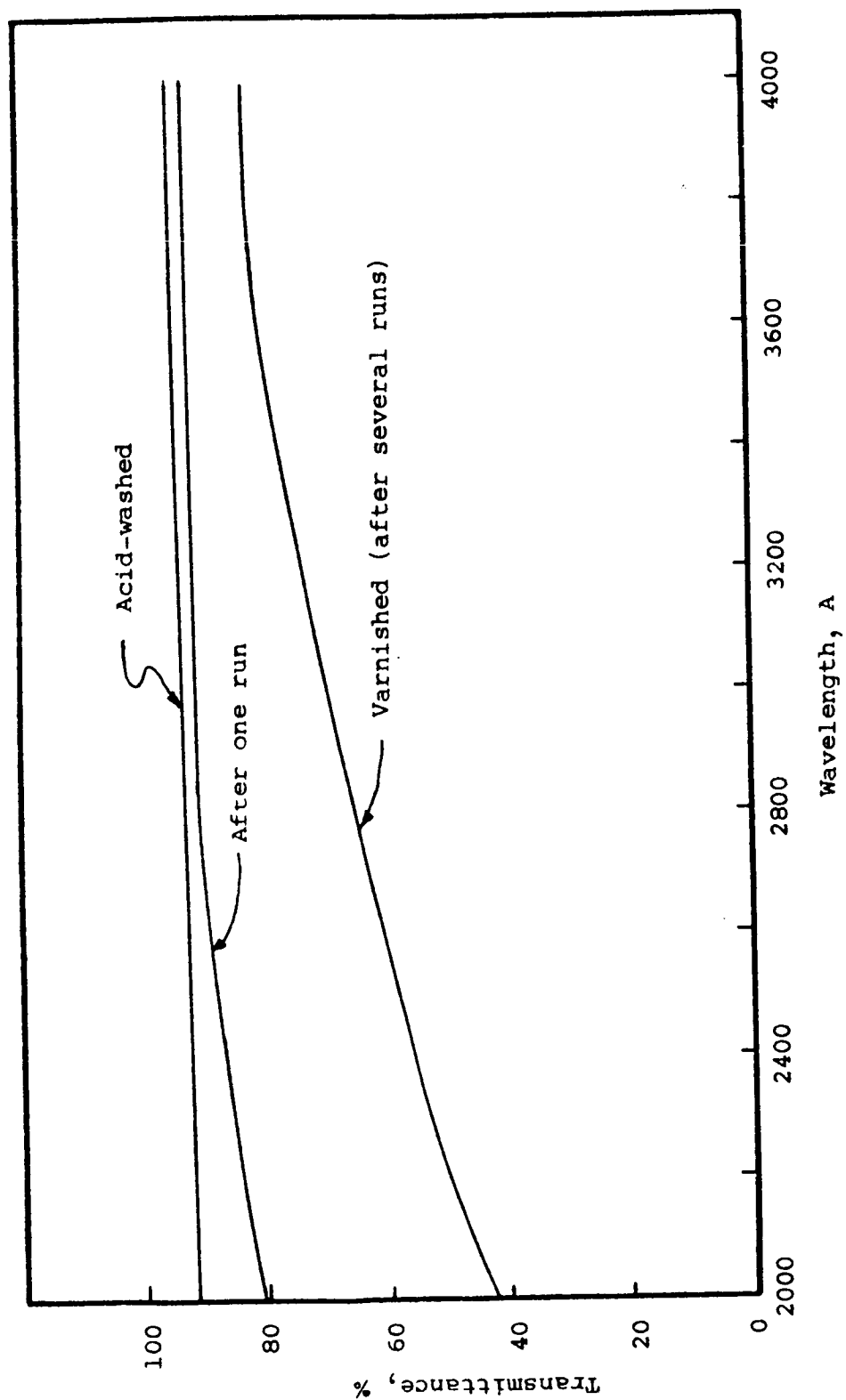


Figure 10
TRANSMITTANCE LOSSES DUE TO VARNISH FORMATION
ON THE QUARTZ WINDOW

IV. PIGMENT SCREENING

A. Preparation of Samples

The prerequisites for selection of pigments were that they be white and of high refractive index and purity. The most important factor in the choice of materials, i.e., stability to the space environment, was determined by screening tests and from limited information in the literature. The search for pigment materials was a continuous activity during this program.

For preliminary screening tests, the samples were prepared as compacted powders that were suitable for both solar-simulation exposure and optical measurements. The candidate powder was poured into a copper ring, 1-1/2-inch ID, placed on a vellum-covered steel plate. A steel disk of 1-1/2-inch diameter was fitted into the ring, covering the pigment. Applying a pressure of 10,000 psi on the disk resulted in the finished specimen illustrated in Figure 11. No binders or lubricants were used, thus avoiding possible effects of foreign materials. Powders which were not compactable into a cohesive body were placed in aluminum dishes for solar exposure. This procedure precluded optical measurements and permitted only visual observation of color change.

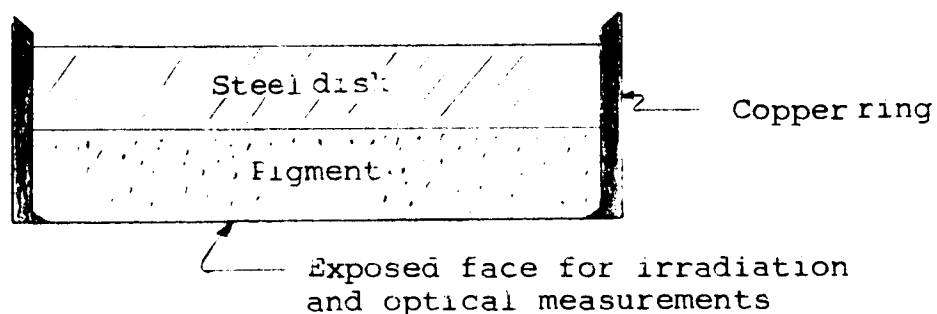


Figure 11

PIGMENT SAMPLE

B. Irradiation

Most of the pigments were exposed to ultraviolet irradiation in vacuum in the oil-diffusion-pumped system with the internally mounted lamps. Two exceptions were Rokide A (alumina) and AlSiMag 243 (forsterite), which were tested in the system with the externally mounted lamp. Zinc oxide powders were exposed to more than 1000 ESH in the ion-pumped system.

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C. Results

1 General

Considerable coloration occurred in most of the pigments, as shown in Table 3. Representative reflectance values are given for two wavelengths in the visible spectrum, 440 and 600 mμ. For most of the early screening work, reflectance curves in the visible spectrum were sufficient to suggest or preclude additional study.

In general, natural, mined minerals were less affected by ultraviolet irradiation in vacuum than synthetic laboratory chemicals. Exceptions were zinc compounds and tin oxide. For example, natural wollastonite was superior to synthetic calcium silicate. Calcination of hydrated materials to their anhydrous forms enhanced stability, as evidenced by the kaolins and talc. Calcination at 1000°C for 16 hours of alumina, zirconia, and zircon, however, had little effect on their stability. Apparently any loss of adsorbed or absorbed water and the possible strain relief gained by thermal treatment did not change the degradation characteristics of these materials. A marked difference in stability was apparent among different crystal forms of the same material. Metastable gamma alumina and cubic (unstabilized) zirconia degraded much more severely than their stable counterparts, alpha alumina and monoclinic zirconia. Materials other than zinc oxide which were fairly stable were zinc sulfide, stannic oxide, diatomaceous earth (amorphous silica), and fired kaolin (mullite plus amorphous silica). Although AlSiMag 243 (forsterite) also exhibited good stability, its low initial reflectance precluded further study.

Changes in reflectance curves in the visible spectrum for pigments ranging from excellent (zinc oxide) to poor (antimony oxide) are presented in Figures 12 through 15. For practically all materials the reflectance losses were smallest at the longer wavelengths and increasingly greater at the shorter wavelengths.

Table 3

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF MISCELLANEOUS INORGANIC PIGMENTS

| Material | Manufacturer's Designation | Supplier | Exposure | | Reflectance, % | |
|---|----------------------------|----------------------------------|----------|--------------|----------------|---------------|
| | | | ESH | Solar Factor | 440 mμ | 600 mμ |
| $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ | | Victor Chemical | 0 180 | 3 | 97.5 61.5 | 96.5 80.0 |
| Al_2O_3 | Alucer MC (alpha) | Gulton Industries | 0 180 | 3 | 100.0 74.0 | 100.0 91.5 |
| Al_2O_3 | Alucer MA (gamma) | Gulton Industries | 0 75 | 1.5 | 93.5 49.5 | 90.0 82.5 |
| Al_2O_3 | Rokide A (flame-sprayed) | Norton | 0 615 | 8.9 | 85.5 70.0 | 87.5 84.0 |
| $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ | Ajax P kaolin | Georgia Kaolin | 0 180 | 3 | 73.0 46.5 | 84.5 60.0 |
| $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | Ajax SC kaolin | Georgia Kaolin | 0 200 | 3 | 78.0 65.0 | 87.0 81.0 |
| $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | Mullite | Carborundum | 0 200 | 3 | 90.0 69.0 | 91.0 86.5 |
| $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 3\text{SiO}_2$ | Superfine Molochite | Paper Makers Importing Co. | 0 180 | 3 | 84.5 75.5 | 86.5 84.5 |
| Sb_2O_3 | | National Lead | 0 75 | 1.5 | 92.5 36.5 | 96.5 50.0 |
| BaCO_3 | Reagent grade | Allied Chemical | 0 200 | 3 | 98.5 71.0 | 99.0 93.5 |
| BN | HC 0021 | Carborundum | 0 75 | 1.5 | 88.5 65.0 | 92.5 84.0 |
| CaCO_3 | Calcite | Whittaker, Clark, and Daniels | 0 180 | 3 | 89.0 70.5 | 93.5 89.5 |
| CaF_2 | Reagent grade | Allied Chemical | 0 200 | 3 | 94.5 61.0 | 97.0 87.5 |
| CaSiO_3 | Synthetic | Johns-Manville | 0 75 | 1.5 | 86.0 58.0 | 90.0 81.0 |

| | | | | | | |
|--|--|----------------------------------|-----------|-----|--------------|--------------|
| CaSiO ₃ | Wollastonite C-1 | Cabot | 0 75 | 1.5 | 92.5 81.0 | 94.5 91.5 |
| Casio ₃ | Wollastonite C-6 | Cabot | 0 180 | 3 | 92.0 70.0 | 93.5 86.5 |
| La ₂ O ₃ | Code 528 (calcined 16 hr at 1000°C) | Lindsay Chemical | 0 180 | 3 | 89.0 73.0 | 94.5 90.5 |
| 2PbCO ₃ ·Pb(OH) ₂ | | National Lead | 0 75 | 1.5 | 93.5 52.0 | 96.0 80.5 |
| Basic silicate white lead | 45x | National Lead | 0 75 | 1.5 | 88.5 66.5 | 91.5 82.5 |
| MgAl ₂ O ₄ | Spinel | Linde | 0 75 | 1.5 | 97.5 70.0 | 97.0 92.5 |
| MgO | Reagent-grade powder | Mallinckrodt | 0 75 | 1.5 | 98.5 71.0 | 98.5 92.5 |
| MgO | Sintered piece | Corning Glass | 0 300 | 3 | 83.0 61.0 | 96.0 84.5 |
| MgSiO ₃ ·nH ₂ O | No. 140 Alabama talc | Whittaker, Clark, and Daniels | 0 180 | 3 | 89.0 62.0 | 92.0 73.5 |
| 2MgC·SiO ₂ | AlSi Mag 243 | American Lava | 0 1036 | 15 | 33.0 35.5 | 59.0 60.0 |
| Magnesium trisilicate | USP | Mallinckrodt | 0 200 | 3 | 97.5 18.5 | 99.0 44.5 |
| K ₂ O·F ₂ O ₅ | | Victor Chemical | 0 190 | 3 | 99.5 65.0 | 99.0 87.5 |
| SiO ₂ | Ottawa special | Ottawa Silica | 0 75 | 1.5 | 88.5 77.5 | 92.5 90.0 |
| SiO ₂ | Diatomaceous earth, Dicalite WB-5 | Great Lakes Carbon | 0 180 | 3 | 92.0 87.5 | 93.5 93.0 |
| SiO ₂ | No. 7900 Vycor | Corning Glass | 0 200 | 3 | 94.0 43.0 | 95.0 44.5 |
| SnO ₂ | CP | Fisher | 0 300 | 3 | 88.0 78.5 | 90.0 88.0 |

Table 3 (cont.)

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF MISCELLANEOUS INORGANIC PIGMENTS

| Material | Manufacturer's Designation | Supplier | Exposure | | Reflectance, % | |
|--------------------|----------------------------|----------------------------|----------|--------------|----------------|--------------|
| | | | ESH | Solar Factor | 440 mμ | 600 mμ |
| ZrO ₂ | HP | Titanium Alloy Mfg. | 0 75 | 1.5 | 92.5 65.5 | 97.0 90.5 |
| ZrO ₂ | CP | Titanium Alloy Mfg. | 0 75 | 1.5 | 96.0 75.5 | 97.5 92.5 |
| ZrO ₂ | CP | Fairmount | 0 75 | 1.5 | 89.0 68.0 | 95.0 90.0 |
| ZrO ₂ | CP | Titanium-Zirconium | 0 180 | 3 | 88.0 65.5 | 90.5 80.0 |
| ZrO ₂ | CNC-6-CP | Carborundum | 0 180 | 3 | 93.5 49.0 | 97.0 72.5 |
| ZrO ₂ | Cubic | Titanium Alloy Mfg. | 0 180 | 3 | 88.0 33.0 | 95.5 73.5 |
| ZrSiO ₄ | Milled zircon | Titanium Alloy Mfg. | 0 75 | 1.5 | 87.0 80.0 | 93.5 91.0 |
| ZrSiO ₄ | Superpax | Titanium Alloy Mfg. | 0 180 | 3 | 96.5 65.0 | 92.5 84.5 |
| ZrSiO ₄ | Superpax A | Titanium Alloy Mfg. | 0 180 | 3 | 85.5 64.0 | 90.5 82.5 |
| ZrSiO ₄ | Superpax A (HCl-leached) | Titanium Alloy Mfg. | 0 180 | 3 | 89.0 57.0 | 92.5 75.5 |
| ZrSiO ₄ | CP | Titanium-Zirconium | 0 180 | 3 | 75.5 55.5 | 84.0 71.5 |
| ZrSiO ₄ | Ultrax 1000W | Metal-Thermit | 0 75 | 1.5 | 86.0 78.0 | 93.5 90.5 |
| ZnS | Reagent grade | Matheson, Coleman and Bell | 0 75 | 1.5 | 91.0 89.0 | 94.5 94.0 |

The following materials were irradiated in the environmental chamber as loose powders because they could not be compacted. Visually observed color changes are reported in lieu of instrumental measurements.

| | | | | | |
|--|---|-------------------------------|-----|-----|----------|
| $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ | | Monsanto | 180 | 3 | Moderate |
| $\text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ | C8675 | Victor Chemical | 200 | 3 | Strong |
| $\text{CaO} \cdot \text{P}_2\text{O}_5$ | | Victor Chemical | 180 | 3 | Strong |
| Feldspar | | Keystone | 180 | 3 | Moderate |
| $\text{Li}_2\text{O} \cdot \text{TiO}_2$ | | Lithium Corp. of America | 180 | 3 | Moderate |
| $4\text{Li}_2\text{O} \cdot 3\text{ZrO}_2 \cdot 5\text{SiO}_2$ | | Metalloy Corp. | 180 | 3 | Moderate |
| $\text{MgSiO}_3 \cdot n\text{H}_2\text{O}$ | | International Talc | 180 | 3 | Moderate |
| MgSiO_3 | No. 140 Alabama talc (1200°C for 2 hr in N_2) | Whittaker, Clark, and Daniels | 180 | 3 | Moderate |
| MgSiO_3 | No. 140 Alabama talc (1200°C for 15 hr in air) | Whittaker, Clark, and Daniels | 200 | 3 | Moderate |
| SiO_2 | Cristobalite | Harbison-Walker | 180 | 3 | Moderate |
| SiO_2 | Quso | Philadelphia Quartz | 200 | 3 | Strong |
| SiO_2 | Quso (1200°C for 15 hr in air) | Philadelphia Quartz | 200 | 3 | Moderate |
| SrTiO_3 | | Titanium Alloy Mfg. | 75 | 1.5 | Moderate |
| TiO_2 | Titanox TG | Titanium Alloy Mfg. | 75 | 1.5 | Strong |
| $\text{ZnO} \cdot \text{TiO}_2$ | | | 200 | 3 | Strong |

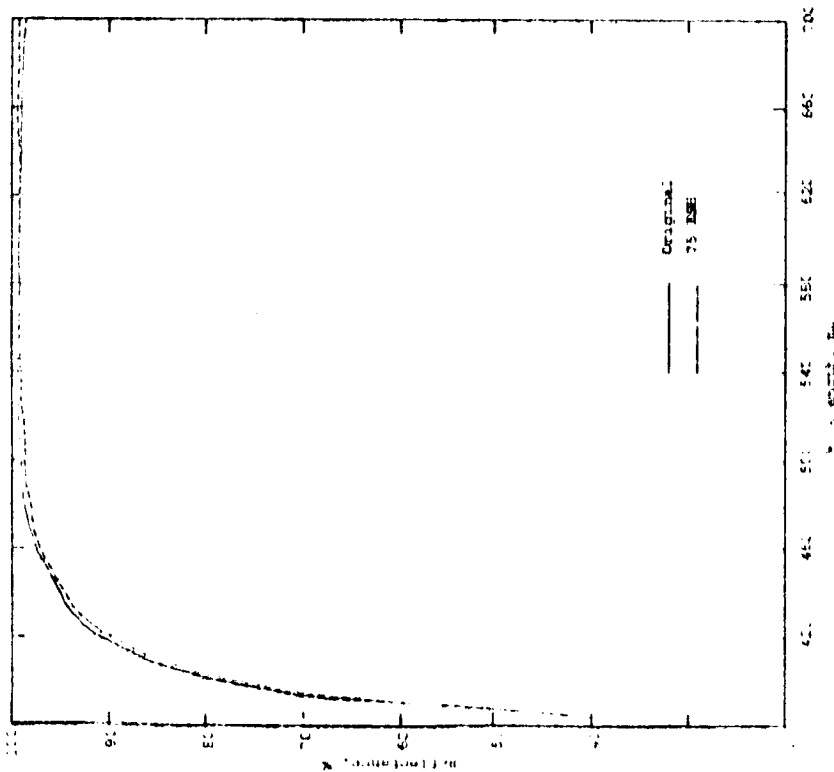


Figure 12

EFFECT OF 75 ESH IN VACUUM ON VISIBLE
SPECTRAL REFLECTANCE OF ZINC OXIDE

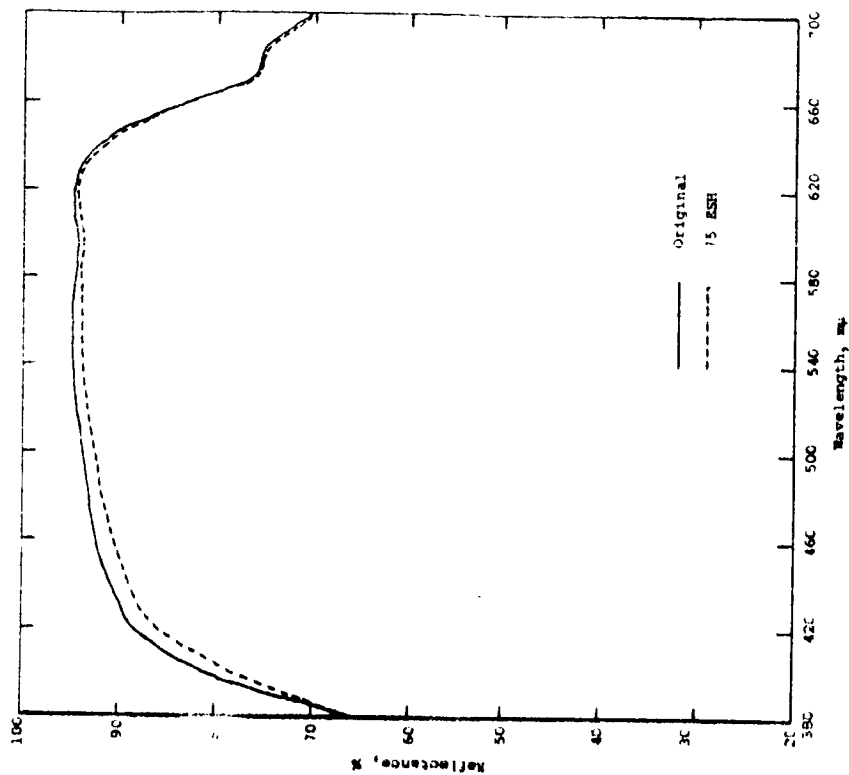


Figure 13

EFFECT OF 75 ESH IN VACUUM ON VISIBLE
SPECTRAL REFLECTANCE OF ZINC SULFIDE

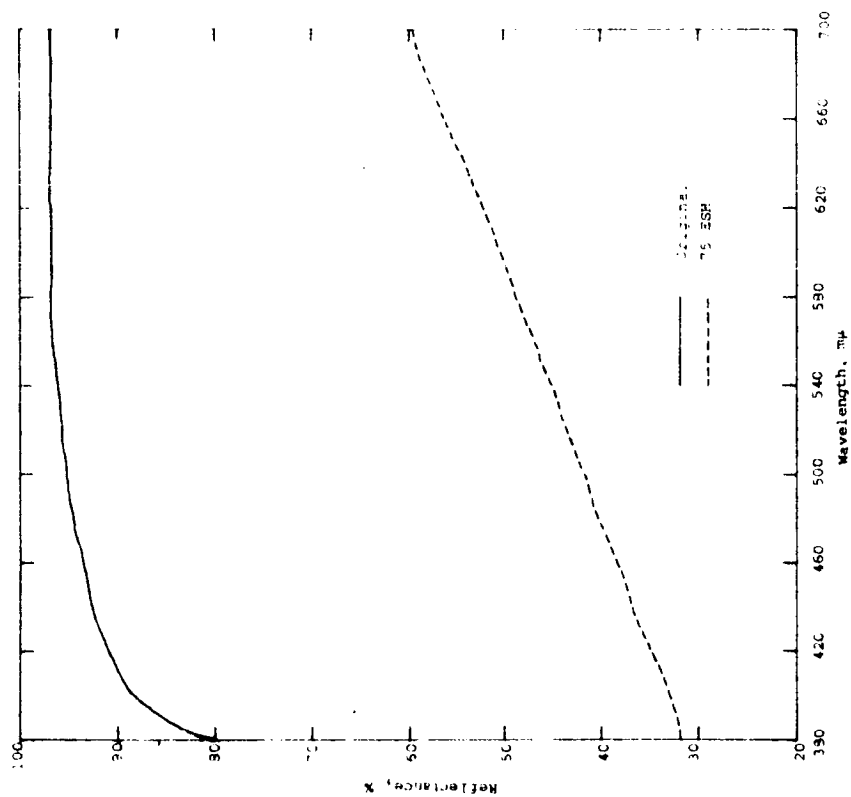


Figure 14

EFFECT OF 75 ESH IN VACUUM ON VISIBLE
SPECTRAL REFLECTANCE OF ZIRCONIUM OXIDE

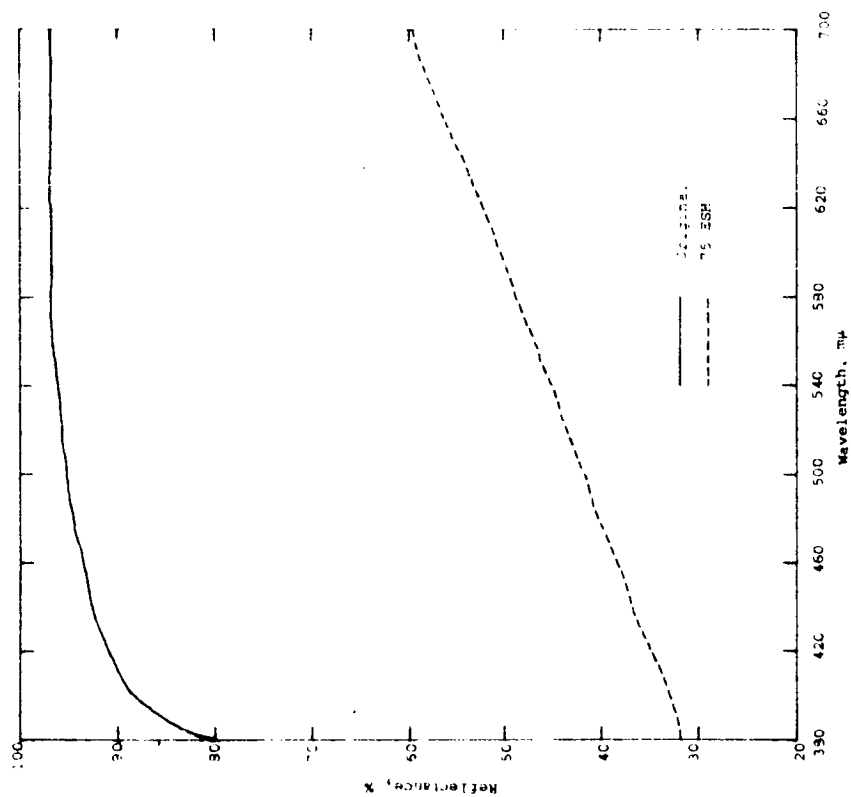


Figure 15

EFFECT OF 75 ESH IN VACUUM ON VISIBLE
SPECTRAL REFLECTANCE OF ANTIMONY OXIDE

2. Zinc Oxide

The properties of the zinc oxide powders investigated appear in Table 4.

Table 4

PROPERTIES OF ZINC OXIDE PIGMENTS INVESTIGATED

| <u>Manufacturer s</u> <u>Designation</u> | <u>Supplier</u> | <u>Purity,*</u> <u>%</u> | <u>Mean</u> <u>Particle</u> <u>Size, μ</u> | <u>Remarks</u> |
|---|-----------------|-----------------------------|---|-----------------------|
| SP 500 | New Jersey Zinc | 99.90 | 0.25-0.35 | |
| USP 12 | New Jersey Zinc | 99.80 | 0.30 | |
| XX 504 | New Jersey Zinc | 99.60 | 1.5 | |
| XX 254 | New Jersey Zinc | 99.60 | 1.5 | Felleted |
| AZO-33 | American Zinc | 99.20 | 0.20 | Acicular |
| AZO-55LO | American Zinc | 99.20 | 0.40 | Low oil absorption |
| AZO-66 | American Zinc | 99.80 | 0.20 | |
| E-P 414 | Eagle-Picher | 99.40 | 1.0 | |
| E-P 730 | Eagle-Picher | 99.50 | 5.4 | |

* Manufacturer's information.

The data in Table 5 show that zinc oxide was clearly the most stable pigment studied, rivaled only by zinc sulfide, tin oxide, and possibly diatomaceous earth (Table 3). The limited number of short-term tests of zinc oxides of different grades did not reveal any significant effects due to purity. Long-term tests at 1670 and 1720 ESH revealed a surprisingly high absorptance change in SP 500 zinc oxide. Good stability was exhibited in the same tests by calcined SP 500 and also by the unfired and fired forms of AZO-55LO zinc oxide.

Figure 16 illustrates the change in solar absorptance of calcined SP 500. The value of calcination of zinc oxide pigments is threefold: stability to simulated space is improved, initial absorptance is lowered, and physical properties are improved. Improvement of stability, observed in SP 500 and AZO-55LO, may be due to both the smaller surface area of the larger calcined particles and the elimination of defects and may also be due in part to volatilization of contaminants. Lowering of the initial absorptance results mainly from reflectance increases in the infrared region; these increases may be due to enhanced scattering

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Table 5
EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF ZINC OXIDE PIGMENTS

| Manufacturer's Designation | Treatment | Exposure | | Reflectance, % | | Solar Absorbance | | |
|----------------------------|-------------------------|----------|--------------|----------------|--------|------------------|----------------|------|
| | | ESH | Solar Factor | 440 mμ | 600 mμ | a ₁ | a ₂ | Δa |
| SP 500 | | 0 | | 95.0 | 99.0 | | | |
| | | 75 | 1.5 | 95.0 | 99.0 | | | |
| AZO-66 | | 0 | | 93.0 | 99.0 | | | |
| | | 200 | 3 | 91.0 | 98.0 | | | |
| USP | | 0 | | 93.0 | 98.5 | | | |
| | | 200 | 3 | 91.5 | 97.5 | | | |
| SP 500 | Calcined 16 hr at 800°C | 0 | | 69.0 | 92.5 | | | |
| | | 300 | 3 | 69.0 | 92.5 | | | |
| USP 12 | | 0 | | 93.5 | 98.0 | | | |
| | | 300 | 3 | 92.0 | 97.5 | | | |
| AZO-33 | | 0 | | 88.0 | 95.0 | | | |
| | | 300 | 3 | 86.5 | 93.5 | | | |
| SP 500 | | 0 | | 95.0 | 99.0 | | | |
| | | 3100 | 10 | 91.0 | 98.0 | | | |
| SP 500 | | 0 | | 92.5 | 97.0 | .096 | .048 | .143 |
| | | 1670 | 9 | 90.0 | 96.0 | .105 | .068 | .173 |
| SP 500 | Calcined 16 hr at 700°C | 0 | | 92.0 | 96.5 | .098 | .039 | .136 |
| | | 1670 | 9 | 92.0 | 97.0 | .097 | .043 | .140 |
| AZO-55LO | | 0 | | 85.5 | 92.0 | .118 | .084 | .202 |
| | | 1670 | 9 | 83.5 | 91.0 | .127 | .085 | .212 |
| SP 500 | | 0 | | 93.5 | 98.0 | .094 | .044 | .138 |
| | | 1720 | 10.2 | 90.5 | 96.0 | .102 | .062 | .164 |
| SP 500 | Calcined 16 hr at 700°C | 0 | | 92.5 | 97.5 | .097 | .036 | .133 |
| | | 1720 | 10.2 | 91.5 | 97.5 | .097 | .043 | .140 |
| AZO-55LO | | 0 | | 86.5 | 93.5 | .116 | .082 | .198 |
| | | 1720 | 10.2 | 83.5 | 92.0 | .126 | .087 | .213 |
| AZO-55LO | Calcined 16 hr at 700°C | 0 | | 90.0 | 95.5 | .106 | .049 | .156 |
| | | 1720 | 10.2 | 88.5 | 95.0 | .110 | .054 | .164 |
| | | | | | | | | .008 |

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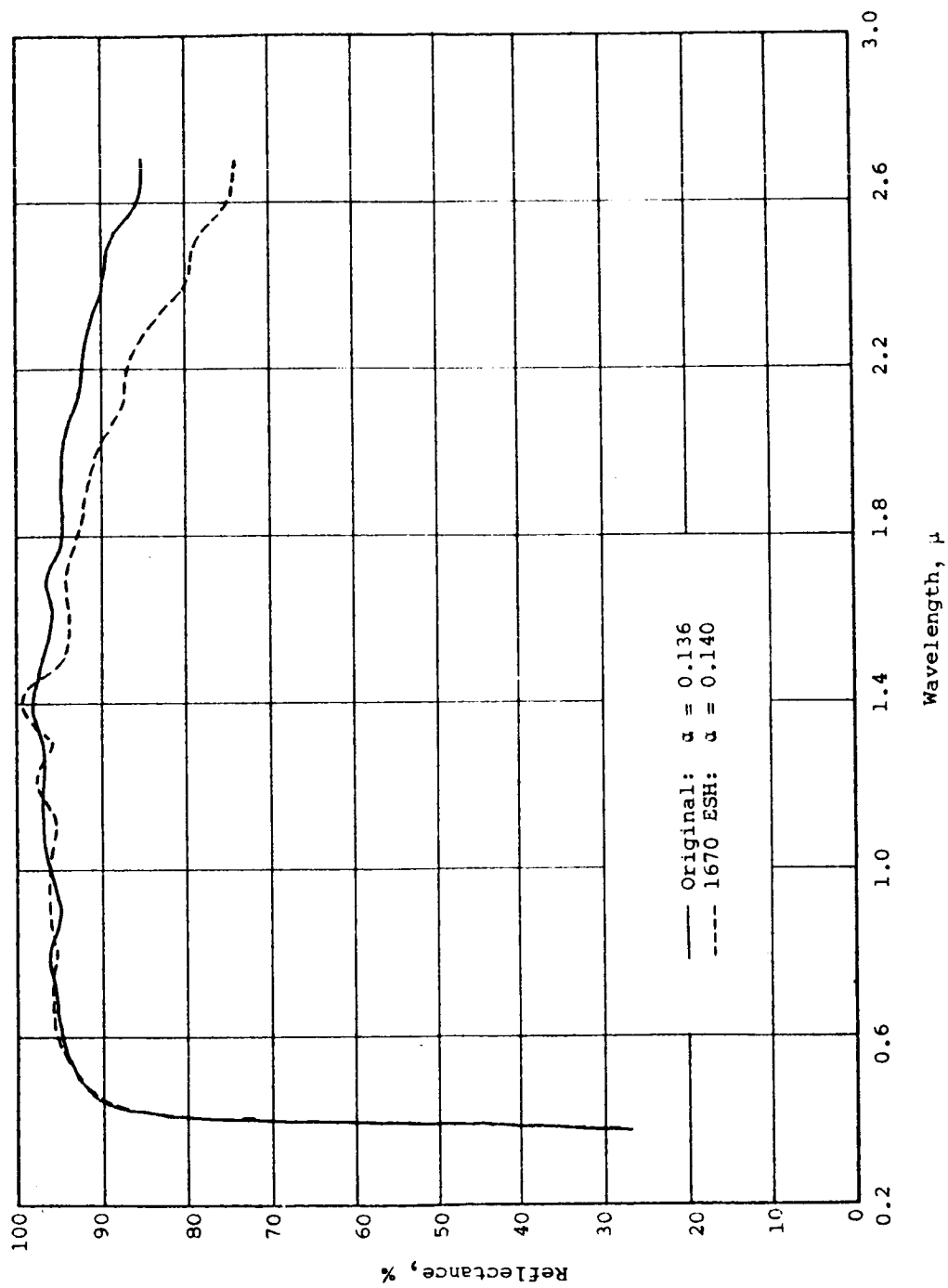


Figure 16

EFFECT OF 1670 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF SP 500 ZINC OXIDE
CALCINED AT 700°C FOR 16 HOURS

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at the longer wavelengths by the larger particles. Better mechanical properties are a result of the lower liquid (diluent or vehicle or both) requirements in the formulation due to the smaller surface area of the larger particles.

Investigation of zinc oxide powders, complemented by paint studies (Sections V and VI) showed that SP 500 calcined at 700°C for 16 hours was the most satisfactory pigment for use in silicate-bonded thermal-control coatings. Although other grades of zinc oxide exhibited optical and physical properties approaching those of SP 500, more consistent performance can probably be expected from SP 500 because of more stringent manufacturing control.

V. SCREENING OF INORGANIC PAINTS

A. Binders

Water-based inorganic binders which were investigated were: a 50% solution of monoaluminum dihydrogen phosphate obtained from Victor Chemical (designated AP in the tables), Ludox colloidal silicas from Du Pont, and the alkali silicates listed in Table 6.

Table 6

PROPERTIES OF ALKALI SILICATE BINDERS INVESTIGATED

| Manufacturer's Designation | Supplier | Solution Conc. % | Mol Ratio $M_2O:SiO_2$ |
|-------------------------------|---------------------|------------------------|---------------------------|
| PS7 | Sylvania | 35.0 | $K_2O:3.30 SiO_2$ |
| Kasil 1 | Philadelphia Quartz | 29.1 | $K_2O:3.92 SiO_2$ |
| S-35 | Philadelphia Quartz | 32.1 | $Na_2O:3.87 SiO_2$ |
| N-silicate | Philadelphia Quartz | 37.6 | $Na_2O:3.22 SiO_2$ |

Samples of PS7, aluminum phosphate, and colloidal silica were prepared as powders by evaporating to dryness and calcining at 800°C. Samples for exposure to ultraviolet radiation in vacuum were prepared by employing the same compacting technique used for pigments. The silica, however, could not be compacted, so it was irradiated as a loose powder. Reflectance losses of 5.5 and 1.5% for the silicate and 21.0 and 11.5% for the phosphate occurred at 440 and 600 mμ after 75 ESH at an intensity of 1.5 suns. The colloidal silica was visually observed to yellow considerably in this same test.

A second and perhaps more valid method of studying the stability of the binders was by their incorporation into paints which were subjected to a simulated space environment. The results for zirconia-pigmented paints C45 to C49, in Table 9, show the inferior stability of colloidal silica-bonded coatings. Phosphate-bonded paints generally exhibited optical property changes similar to those of silicate-bonded samples. No significant effect on stability of zinc oxide paints was noted through the use of different alkali silicates as shown by samples Z13 to Z15 in Table 10.

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As a group, the alkali silicates were preferable to the colloidal silicas from the standpoint of both stability and physical properties. The alkali silicates were also preferable to aluminum phosphate, because its acidity necessitates the use of protective primers on metals and because low-temperature-cured phosphate coatings are sensitive to moisture. Potassium silicate was preferable to sodium silicate because it is less likely to develop carbonate efflorescence.⁵ The final choice of PS7 potassium silicate was dictated by its higher purity and better physical properties in comparison with the other alkali silicates.

B. Paints

All paint formulations contained three ingredients: pigment, binder, and enough water to achieve a sprayable consistency. Maximization of the pigment/binder ratio (PBR) was defined by physical properties. The methods used early in the program for preparation of the formulations were either mixing the constituents by a combination of grinding and mixing action in an agate mortar and pestle, or hand-shaking the composition containing a few porcelain balls. The classical procedure for paint preparation, i.e. ball-milling was used during the bulk of the program.

Spray-painting was done with a Paasche type AUTF airbrush. limited brush-painting was done with conventional camel-hair brushes. Aluminum pieces were grit blasted with 40-mesh silicon carbide prior to paint application to promote adhesion. The thickness of the paint was considered satisfactory when the substrate was adequately covered. Since drying powder is a function of pigment/binder ratio, particle size and refractive indices, the thicknesses varied with the pigments used.

The majority of the paints were irradiated in the oil-diffusion-pumped system with the internally mounted lamps. A few of the more promising compositions were subjected to longer tests of 450 and 2100 ESH in the ion pumped chambers C7 and C17 in Table 7, C42 in Table 8, and C55 in Table 9.

Test results for a variety of paints appear in Table 7. In this group, tin oxide- and zinc sulfide-pigmented coatings were the only materials which exhibited stability approaching that of zinc oxide paints. However, both compositions had a

⁵Vail, J. G., 'Soluble Silicates', Reinhold Publishing Corp., New York, Vol. II, p. 231, 1952.

Table 7

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF MISCELLANEOUS INORGANIC COATINGS
 All samples cured at 140°C for 18 hr.
 Pigments not described under Remarks are reported in Table 3.

| Sample | Composition | | | Solids Content, % | Remarks | Exposure | | Reflectance, % | | Solar Absorbance | |
|--------|-----------------------|--------|------|-------------------|---|-----------|--------------|----------------|--------------|------------------|-----------------------------|
| | Pigment | Binder | PBR | | | ESH | Solar Factor | 440 mμ | 600 mμ | $\frac{a}{d}$ | $\frac{\Delta a}{\Delta d}$ |
| C1 | $Al_2O_3 \cdot 3H_2O$ | PS7 | 4.30 | 66.2 | Pigment: C-35, Alcoa | 0 180 | 3 | 79.5 58.5 | 80.5 74.0 | | |
| C2 | $Al_2O_3 \cdot 3H_2O$ | PS7 | 4.30 | 63.9 | Pigment: C-35, Alcoa | 0 200 | 3 | 75.5 64.5 | 75.5 72.5 | .345 .371 | .026 |
| C3 | $CaSiO_3$ | PS7 | 4.30 | 62.8 | Pigment: Wollastonite P-1, Cabot | 0 180 | 3 | 78.5 52.5 | 83.5 71.5 | | |
| C4 | La_2O_3 | PS7 | 4.30 | 56.9 | | 0 180 | 3 | 92.5 54.0 | 95.0 77.5 | | |
| C5 | $LiAlSi_4O_{10}$ | PS7 | 4.30 | 64.4 | Pigment: Petalite, Foote Mineral | 0 250 | 2.5 | 59.0 52.0 | 64.5 62.5 | | |
| C6 | $LiAlSiO_4$ | PS7 | 4.30 | 64.4 | Pigment: experimental material, Foote Mineral | 0 250 | 2.5 | 86.5 81.5 | 85.5 84.5 | | |
| C7 | $LiAlSiO_4$ | PS7 | 4.30 | 64.4 | Pigment: Lithafrax, Carborundum | 0 2100 | 10 | 85.0 43.5 | 86.0 60.5 | | |
| C8 | $MgAl_2O_4$ | PS7 | 1.50 | 37.9 | | 0 75 | 1.5 | 93.5 76.0 | 98.0 94.5 | | |
| C9 | $MgSiO_3$ | PS7 | 4.30 | 56.9 | Brush-painted | 0 200 | 3 | 92.5 66.5 | 94.5 84.0 | .130 .219 | .089 |

| | | | | | | | | | | | |
|-----|------------------|-----|------|------|--|-----------|-----|--------------|--------------|--------------|------|
| C10 | SiO ₂ | PS7 | 4.30 | 64.4 | Pigment: fused silica, Glassrock | 0 200 | 3 | 71.5 60.5 | 76.0 72.0 | .295 .329 | .034 |
| C11 | SiO ₂ | PS7 | 4.30 | 62.8 | Pigment: fused quartz powder, General Electric | 0 300 | 3 | 87.0 76.0 | 87.5 85.0 | .177 .221 | .044 |
| C12 | SiO ₂ | PS7 | 4.30 | 62.8 | Pigment: fused quartz crystal, General Electric | 0 70 | 3 | 67.5 64.0 | 70.0 68.0 | .346 .376 | .030 |
| C13 | SnO ₂ | PS7 | 4.30 | 61.7 | | 0 300 | 3 | 77.0 76.5 | 82.5 82.0 | .264 .278 | .014 |
| C14 | SnO ₂ | PS7 | 4.30 | 61.7 | Applied on glass slide | 0 250 | 2.5 | 80.5 80.5 | 87.5 88.5 | | |
| C15 | SnO ₂ | AP | 4.20 | 57.8 | Applied on glass slide | 0 250 | 2.5 | 69.5 65.5 | 76.5 75.0 | | |
| C16 | SnO ₂ | PS7 | 4.30 | 52.9 | Pigment: prime metal, Metal-Thermit | 0 250 | 2.5 | 77.5 74.5 | 82.0 81.0 | | |
| C17 | SnO ₂ | PS7 | 4.30 | 61.7 | | 0 2100 | 10 | 76.5 67.0 | 83.0 78.5 | | |
| C18 | ZnS | PS7 | 3.19 | 59.0 | | 0 260 | 4 | 85.0 81.0 | 90.5 88.5 | .220 .231 | .011 |
| C19 | ZnS | PS7 | 4.30 | 56.9 | Pigment: XXXN, Chas. Osborne Co. | 0 250 | 2.5 | 88.5 86.5 | 88.0 87.5 | | |
| C20 | ZnS | PS7 | 3.19 | 59.0 | Pigment: XXXN, Chas. Osborne Co. | 0 250 | 2.5 | 88.5 86.5 | 89.0 88.5 | | |
| C21 | ZnS | PS7 | 4.30 | 56.9 | Pigment: XXXHD, Chas. Osborne Co. | 0 250 | 2.5 | 88.5 86.0 | 90.0 90.5 | | |

higher solar absorptance than zinc oxide paints. Also, difficulties were encountered in achieving coatings of good physical properties. These drawbacks suggested that tin oxide and zinc sulfide be relegated to backup pigments. Solar absorptance curves for these paints and for a degradable system, magnesium silicate-PS7 potassium silicate, appear in Figures 17, 18, and 19.

Diatomaceous earth and fired kaolin were relatively stable in the pigment screening studies. Optical data for paints incorporating these pigments are tabulated in Table 8. Diatomaceous earths from two suppliers were used: Dicalites from Great Lakes Carbon and Celites from Johns-Mansville. These silica products have a low refractive index (1.46) and are widely used in the paint industry as extender pigments. Their use as prime pigments in the alkali silicate systems required very thick coatings, in excess of 10 mils, to achieve opacity. Due to the high surface area and the low bulk density of the diatomaceous earth pigments, copious amounts of water were necessary for formulating sprayable consistencies. The low solids content of the compositions, as seen in Table 8, attest to this particle shape phenomenon of diatomaceous earths. Poor stability was exhibited by the paints incorporating this form of silica, in contrast to the favorable data for the pigment alone. Reflectance changes of a representative paint are illustrated in Figure 20. The poor physical properties also suggested elimination of these materials from extensive study.

Molochite is a highly calcined aluminum silicate produced from a kaolin low in iron and alkali. It is essentially crystalline mullite plus a small amount of amorphous silica. Fairly low reflectance changes due to ultraviolet irradiation in vacuum were observed for the various grades of Molochite. The #6, which is a coarser grade than Superfine (SF), exhibited the best stability. Figure 21 shows the reflectance curve for a #6 paint. Since more extensive grinding would be necessary to obtain the finer material, greater quantities of grinding impurities may exist in the SF. Acid leaching of #6 appeared beneficial to its stability. However, the long-term test (2100 ESH) produced a fair amount of degradation in the paint pigmented with this material.

Table 9 contains data on paint pigmented with zirconium compounds. Although the reflectance changes in the short test (75 ESH) indicated fair stability, later experiments revealed that zirconia-pigmented paints were unsatisfactory. Limited tests showed that coatings incorporating zircon were relatively unstable, as illustrated graphically in Figure 22.

Of the non-zinc oxide paints, only three compositions were relatively stable: those containing zinc sulfide, stannic oxide, or Molochite #6.

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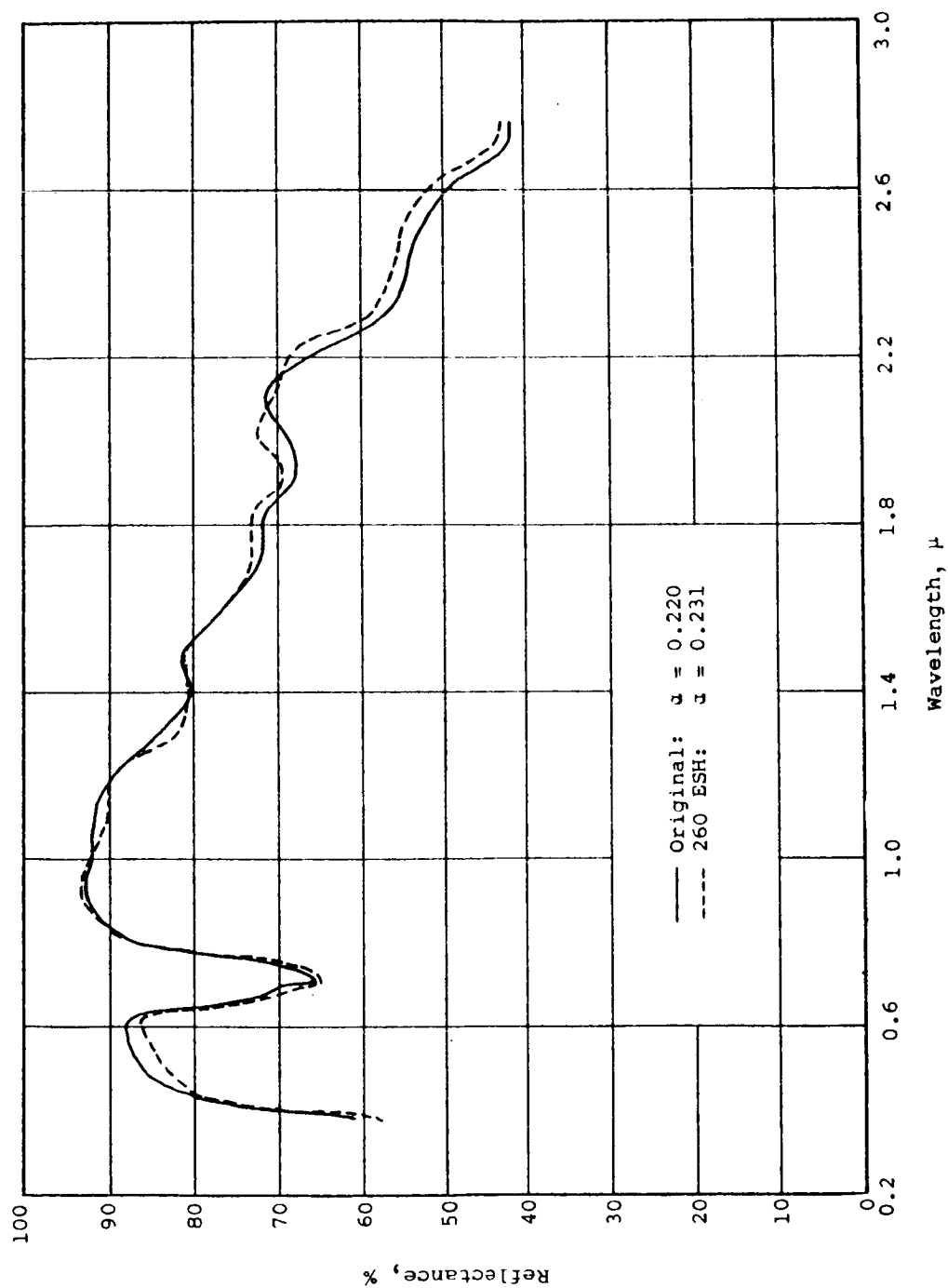


Figure 17
EFFECT OF 260 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
OF ZINC SULFIDE-PS7 COATING (SAMPLE C18)

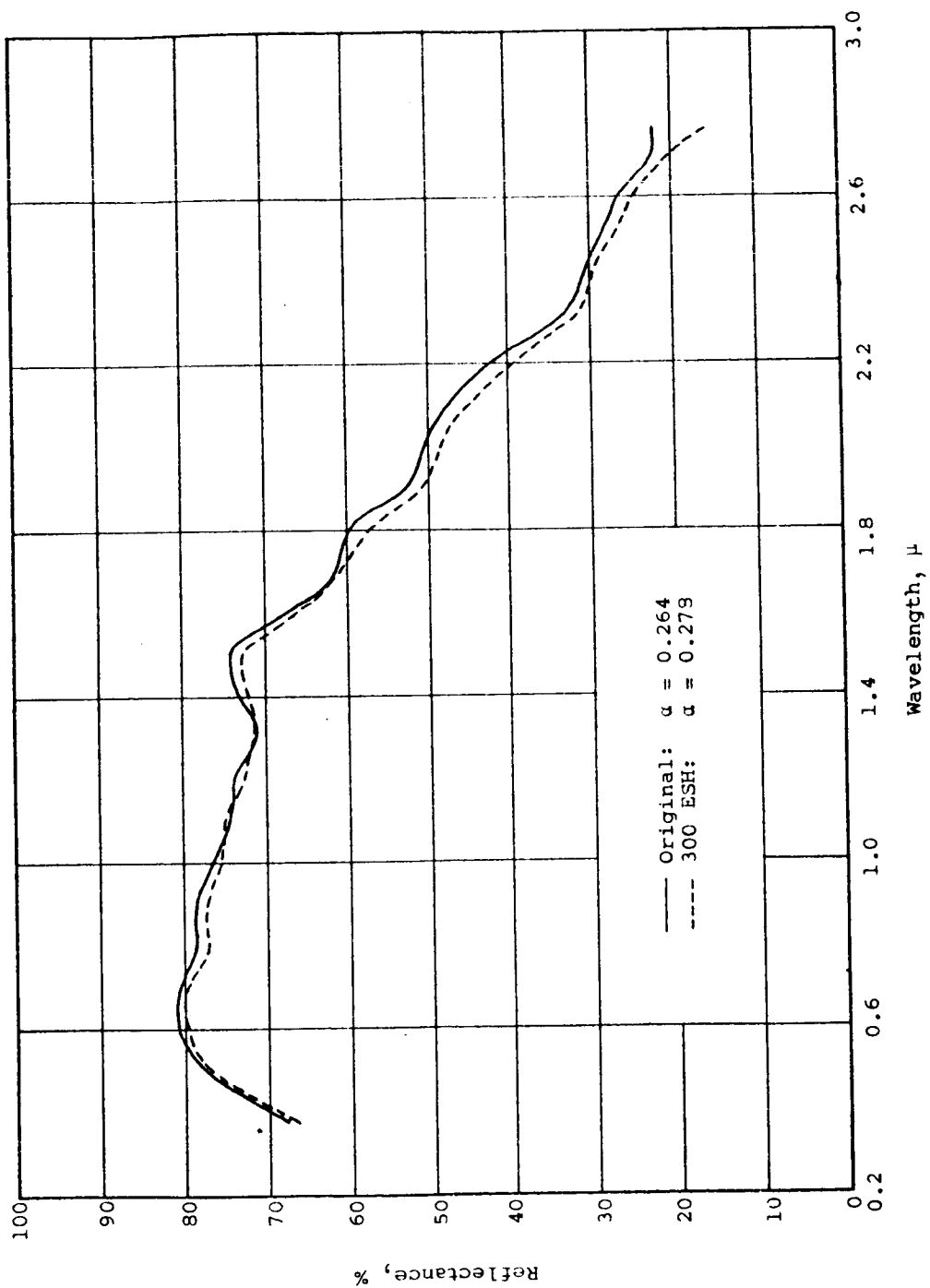


Figure 18

EFFECT OF 300 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
OF TIN OXIDE-157 COATING (SAMPLE C13)

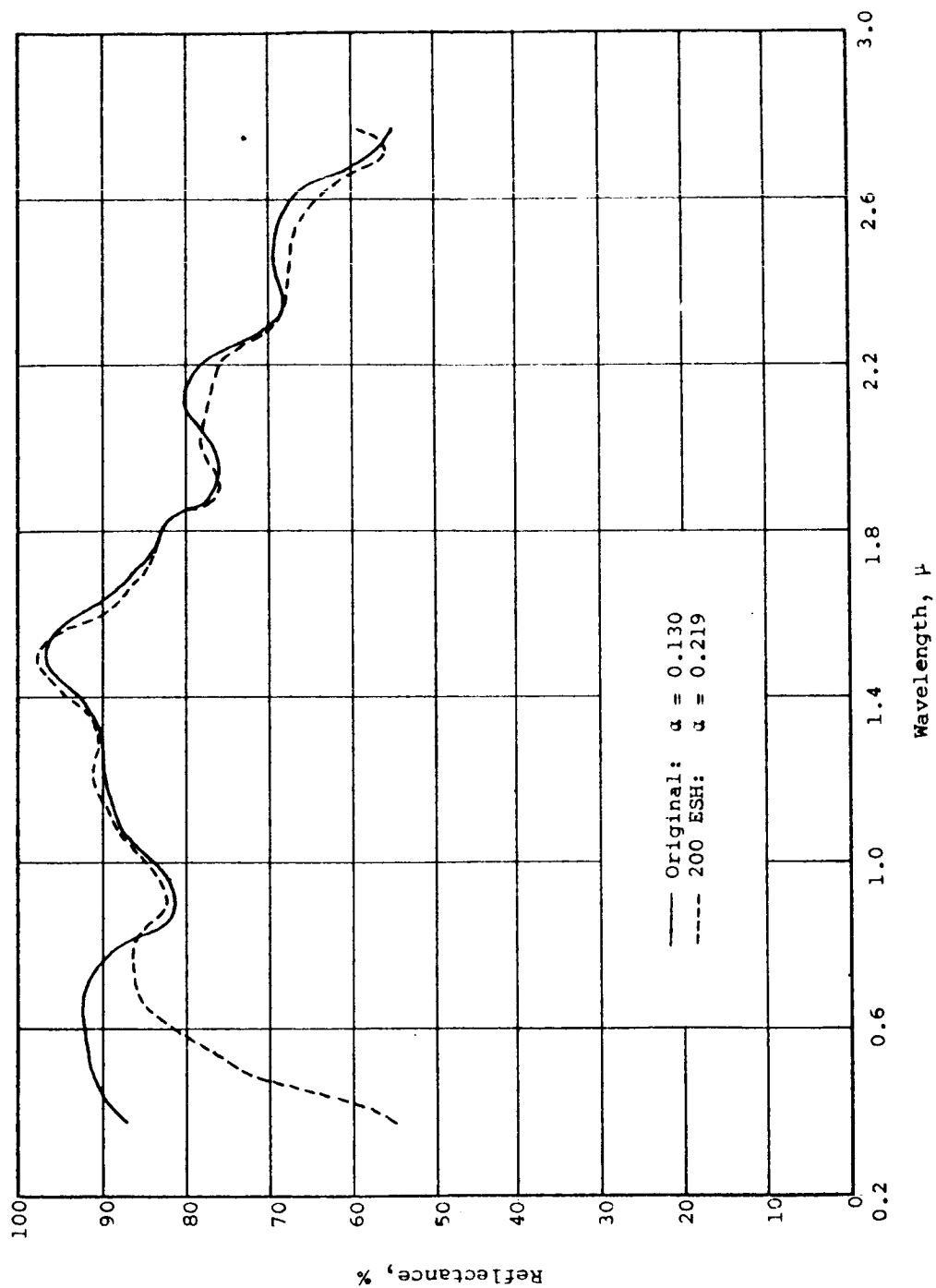


Figure 19
EFFECT OF 200 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
OF MAGNESIUM SILICATE-PS7 COATING (SAMPLE C9)

Table 8

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF INORGANIC COATINGS
 PIGMENTED WITH DIATOMACEOUS EARTH AND FIRED KAOLIN
 All samples cured at 140°C for 18 hr.

| Sample | Composition | | | Solids Content, % | Remarks | Exposure | | Reflectance, % | | Solar Absorbance | |
|--------|---------------|--------|------|-------------------------|---|----------|-----------------|----------------|--------------|---------------------|---------------------------------|
| | Pigment | Binder | PBR | | | ESH | Solar Factor | 440 mμ | 600 mμ | $\frac{1}{\lambda}$ | $\frac{\Delta\lambda}{\lambda}$ |
| C22 | Dicalite WB-5 | PS7 | 1.07 | 34.3 | Diatomaceous earth, Great Lakes Carbon | 0 200 | 3 | 84.5 71.5 | 88.5 83.5 | .186 .229 | .043 |
| C23 | Dicalite WB-5 | PS7 | 2.13 | 30.4 | | 0 300 | 3 | 90.0 77.0 | 91.5 88.5 | .136 .173 | .037 |
| C24 | Dicalite WB-5 | PS7 | 2.13 | 30.4 | Coating cured 16 hr at 425°C | 0 300 | 3 | 91.5 82.5 | 93.0 91.5 | .117 .152 | .035 |
| C25 | Dicalite WB-5 | PS7 | 4.30 | 26.5 | | 0 300 | 3 | 89.0 73.5 | 91.5 88.0 | .128 .186 | .058 |
| C26 | Dicalite L-5 | PS7 | 2.13 | 30.4 | | 0 300 | 3 | 84.5 78.5 | 88.0 86.0 | .175 .207 | .032 |
| C27 | Dicalite WB-5 | AP | 1.40 | 34.8 | Applied on Leonite organic primer | 0 300 | 3 | 83.0 75.5 | 86.0 83.5 | .206 .228 | .022 |
| C28 | Celite 3F | PS7 | 2.13 | 44.1 | Diatomaceous earth, Johns-Manville | 0 300 | 3 | 87.5 71.5 | 91.5 87.0 | .154 .200 | .046 |
| C29 | Celite 281 | PS7 | 2.13 | 30.4 | | 0 300 | 3 | 84.5 74.0 | 89.0 87.0 | .165 .204 | .039 |
| C30 | Celite 110 | PS7 | 2.13 | 30.4 | | 0 300 | 3 | 86.0 77.5 | 85.5 83.5 | .200 .230 | .030 |

| | | | | | | | | | | |
|-----|---------------------------------|-----|------|------|---|------|-----|------|------|------|
| C31 | Molochite SF | PS7 | 4.30 | 56.9 | | 0 | 3 | 75.5 | 81.5 | .252 |
| | | | | | | 200 | | 60.5 | 75.5 | .326 |
| C32 | Molochite #2 | PS7 | 4.30 | 64.4 | | 0 | 3 | 74.5 | 82.5 | |
| | | | | | | 200 | | 68.5 | 79.5 | |
| C33 | Molochite #6 | PS7 | 4.30 | 64.4 | | 0 | 3 | 74.5 | 82.5 | |
| | | | | | | 200 | | 68.0 | 79.0 | |
| C34 | Molochite SF | PS7 | 4.30 | 56.9 | | 0 | 3 | 77.5 | 81.0 | .251 |
| | | | | | | 300 | | 71.0 | 79.0 | .281 |
| C35 | Molochite SF | AP | 2.80 | 61.2 | Applied on Leonite organic primer | 0 | 3 | 75.5 | 81.5 | .229 |
| | | | | | | 300 | | 73.5 | 82.0 | .240 |
| C36 | Molochite #6 | PS7 | 4.30 | 56.9 | | 0 | 3 | 76.5 | 82.5 | .243 |
| | | | | | | 300 | | 73.5 | 81.5 | .260 |
| C37 | 1 Molochite #6: 1 SP 500 ZnO | PS7 | 4.30 | 52.9 | | 0 | 2.5 | 88.5 | 92.5 | |
| | | | | | | 250 | | 86.5 | 92.0 | |
| C38 | 1 Molochite #6: 3 SP 500 ZnO | PS7 | 4.30 | 52.9 | | 0 | 2.5 | 91.5 | 95.5 | |
| | | | | | | 250 | | 90.0 | 94.5 | |
| C39 | Molochite #6 | PS7 | 4.30 | 61.7 | Pigment leached with HCl | 0 | 2.5 | 74.5 | 83.5 | |
| | | | | | | 250 | | 74.5 | 83.5 | |
| C40 | Molochite #6 | AP | 4.20 | 63.3 | Applied on glass slide | 0 | 2.5 | 65.0 | 76.5 | |
| | | | | | | 250 | | 61.5 | 75.5 | |
| C41 | Molochite #6 | AP | 4.20 | 68.3 | Pigment leached with HCl; brush-painted on glass slide | 0 | 2.5 | 64.5 | 76.5 | |
| | | | | | | 250 | | 61.5 | 75.5 | |
| C42 | Molochite #6 | PS7 | 4.30 | 61.7 | Pigment leached with HCl | 0 | 10 | 75.0 | 84.5 | |
| | | | | | | 2100 | | 63.5 | 76.5 | |

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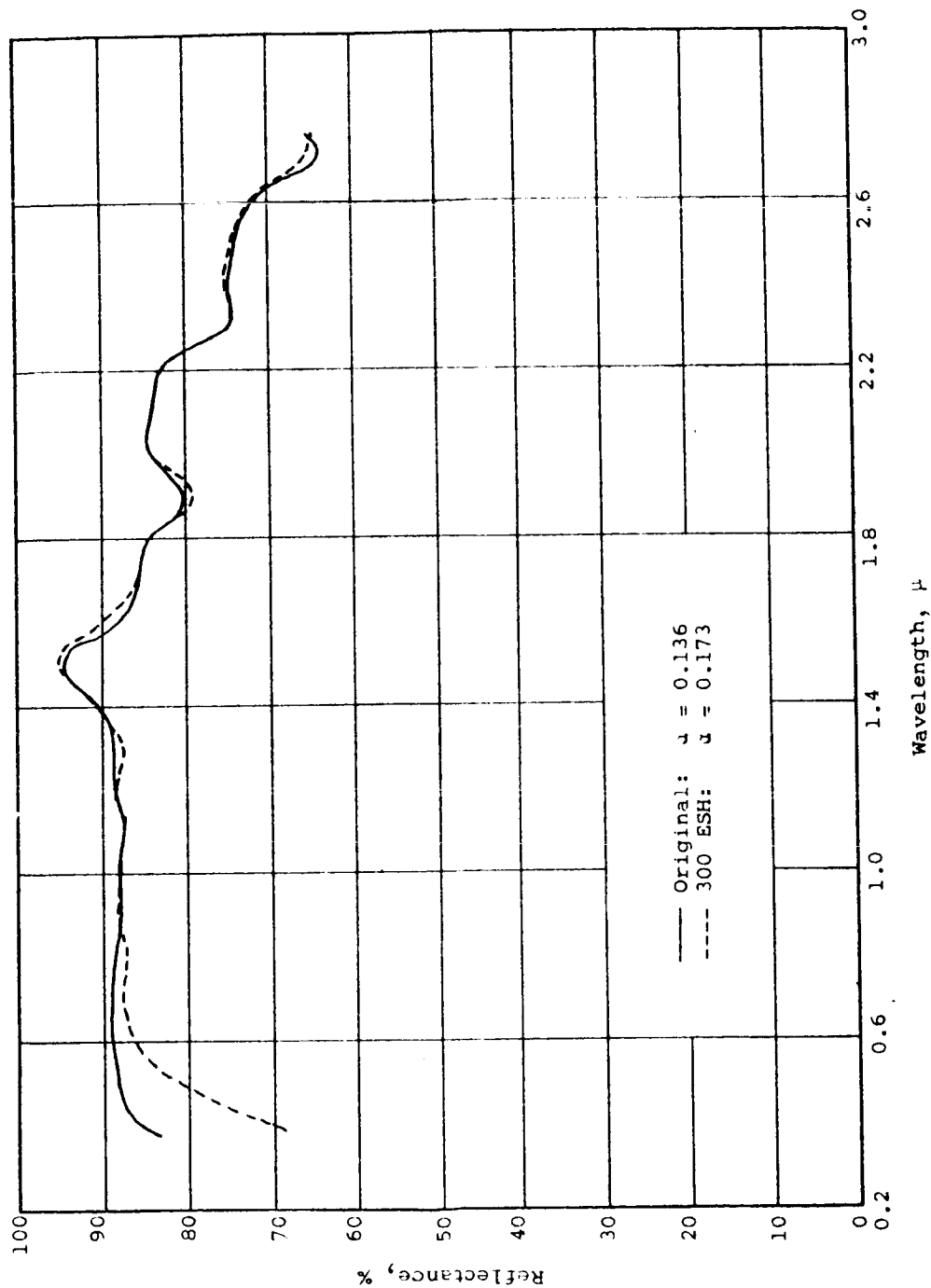


Figure 20

EFFECT OF 300 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
OF DIATOMACEOUS EARTH-PS7 COATING (SAMPLE C23)

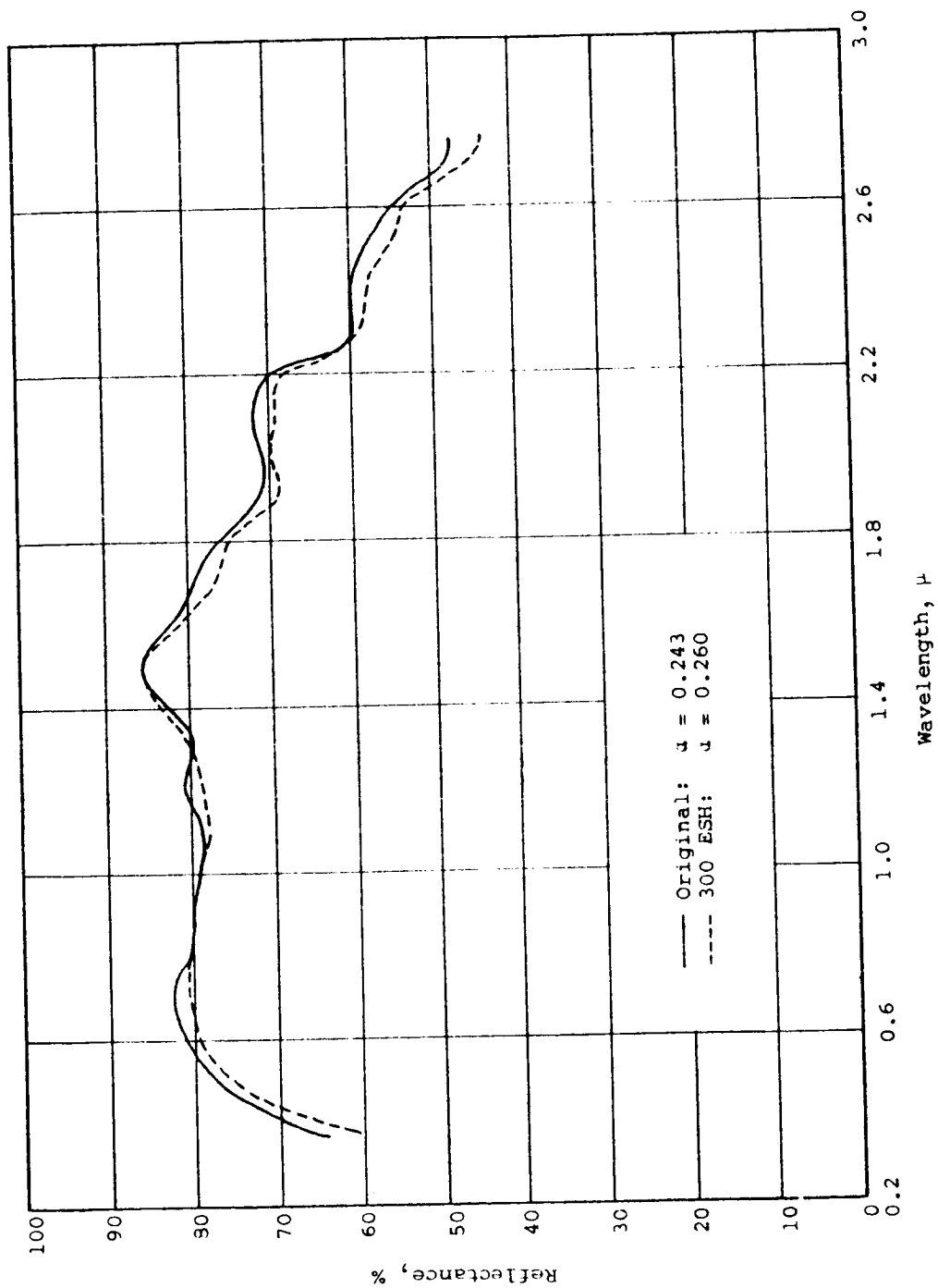


Figure 21
 EFFECT OF 300 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
 OF FIRED KAOLIN-PS7 COATING (SAMPLE C36)

Table 9

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF INORGANIC COATINGS

PIGMENTED WITH ZIRCONIUM COMPOUNDS

All samples cured at 140°C for 18 hr.

All pigments from Titanium Alloy Mfg.

| Sample | Pigment | Composition | | Solids Content, % | Remarks | Exposure | | Reflectance, % | | Solar Absorptance | |
|--------|-----------------------|-------------|------|-------------------|---------------------------|----------|--------------|----------------|--------------|----------------------|----------------------|
| | | Binder | PBR | | | ESH | Solar Factor | 440 mμ | 600 mμ | $\frac{a}{\Delta a}$ | $\frac{b}{\Delta b}$ |
| C43 | ZrO ₂ , HP | PS7 | 4.30 | 73.0 | | 0 75 | 1.5 | 86.0 79.5 | 90.5 87.5 | | |
| C44 | ZrO ₂ , HP | FS7 | 4.30 | 73.0 | | 0 75 | 1.5 | 88.5 83.0 | 94.0 91.5 | | |
| C45 | ZrO ₂ , CP | PS7 | 4.30 | 73.0 | | 0 75 | 1.5 | 89.0 83.5 | 92.0 90.5 | | |
| C46 | ZrO ₂ , CP | AP | 2.80 | 72.0 | Applied on acrylic primer | 0 75 | 1.5 | 76.0 71.5 | 86.0 85.0 | | |
| C47 | ZrO ₂ , CP | Ludox AM | 5.33 | 74.8 | | 0 75 | 1.5 | 89.0 61.5 | 95.5 88.0 | | |
| C48 | ZrO ₂ , CP | Ludox HS | 5.33 | 74.8 | | 0 75 | 1.5 | 91.0 64.5 | 96.5 90.0 | | |

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| | | | | | | | | | |
|-----|----------------------------------|--------------------------------------|------|------|---|-----|-----|------|------|
| C49 | ZrO ₂ , CP | Ludox NH ₃ -stabilized | 5.33 | 74.8 | 0 | 75 | 1.5 | 86.5 | 95.5 |
| | | | | | | | | 63.5 | 88.5 |
| C50 | ZrO ₂ , HP | PS7 | 4.30 | 66.2 | 0 | 180 | 3 | 82.5 | 84.5 |
| | | | | | | | | 67.0 | 79.5 |
| C51 | ZrO ₂ , CP | AP | 2.80 | 70.8 | 0 | 180 | 3 | 88.5 | 90.5 |
| | | Applied on Leonite organic primer | | | | | | 72.0 | 83.5 |
| C52 | ZrO ₂ , CP | PS7 | 4.30 | 64.4 | 0 | 200 | 3 | 90.5 | 93.0 |
| | | | | | | | | 73.5 | 87.0 |
| | | | | | | | | .140 | .205 |
| | | | | | | | | | .065 |
| C53 | ZrO ₂ , CP | AP | 2.80 | 68.4 | 0 | 200 | 3 | 84.5 | 87.5 |
| | | Applied on Leonite organic primer | | | | | | 70.5 | 81.0 |
| | | | | | | | | .156 | .267 |
| | | | | | | | | | .111 |
| C54 | ZrO ₂ , CP | N-silicate | 3.83 | 66.7 | 0 | 200 | 3 | 90.5 | 92.5 |
| | | | | | | | | 77.0 | 87.5 |
| | | | | | | | | .150 | .192 |
| | | | | | | | | | .042 |
| C55 | ZrO ₂ , CP | PS7 | 4.30 | 64.4 | 0 | 450 | 10 | 90.0 | 92.5 |
| | | | | | | | | 82.5 | 89.0 |
| C56 | ZrSiO ₄ , milled | PS7 | 4.30 | 73.0 | 0 | 75 | 1.5 | 75.5 | 83.5 |
| | | | | | | | | 70.5 | 80.5 |
| C57 | ZrSiO ₄ , Superpax | PS7 | 4.30 | 56.9 | 0 | 200 | 3 | 79.0 | 88.5 |
| | | | | | | | | 63.0 | 81.5 |
| | | | | | | | | .180 | .249 |
| | | | | | | | | | .069 |

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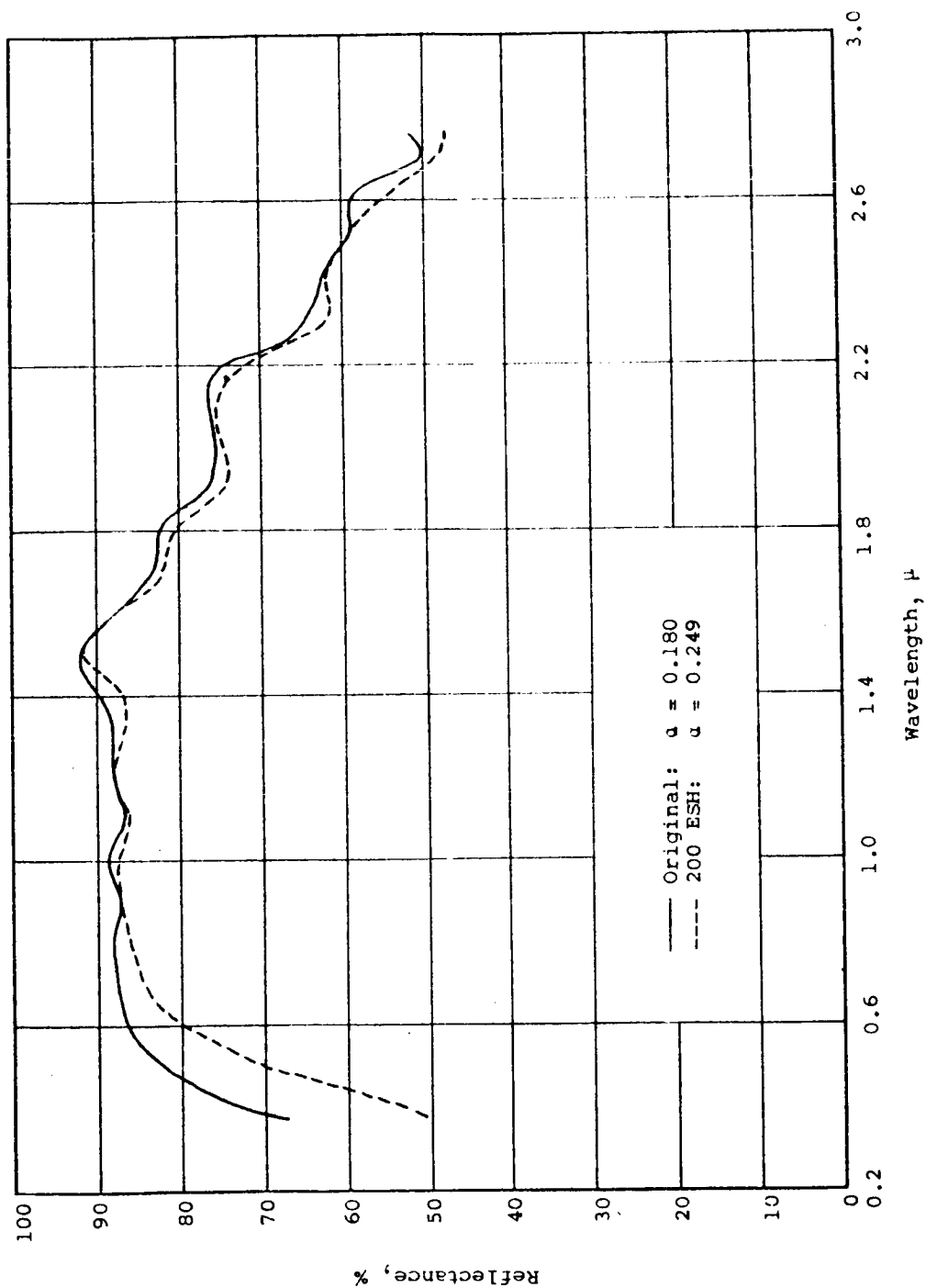


FIGURE 22
 EFFECT OF 200 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
 OF ZIRCONIUM SILICATE-PS7 COATING (SAMPLE C57)

VI. ZINC OXIDE-PIGMENTED ALKALI SILICATE PAINTS

A. Preparation of Materials

1. Formulation

The zinc oxide-pigmented silicate paints were formulated by ball-milling with porcelain balls at about 70% critical speed for 6 to 24 hours. The volume ratio of balls to material was maintained at 1:3 with a total charge of less than 50%. Increasing the ball charge produced a sprayable consistency in a shorter milling time. However, ratios of 1:1 and 2:1 yielded coatings with lower reflectance, decreases of 2 and 6%, respectively, occurred at 440 mμ. This increase in absorptance is attributed to mechanical distortion of the zinc oxide crystal lattice.⁶

Thus it is apparent that keeping the ball charge to a minimum and obtaining more of a mixing rather than a grinding action is necessary for minimum absorptance. The ratio of 1:3 with a total milling time of about 6 hours yields good mixing and sprayability compatible with desirable optical properties for the finished coating.

2. Application

Paints were applied on substrates by spraying with a Paasche type AUTF thumb-action airbrush. Type 6061-T6 aluminum panels, the material generally used for substrates, were abraded with No. 60 Alkoxide metal cloth and thoroughly cleaned with detergent and water. A gas pressure of 30 psi was found to be most suitable. A cylinder of dry compressed air or prepurified nitrogen was used.

The application technique which yielded the best texture and superior physical properties of the coating was: spraying at a distance of 6 to 12 inches until a reflection due to the liquid was apparent, followed by air-drying until the gloss was practically gone, and then repeating the spraying-drying cycle. A thickness of about 1 mil was achieved per cycle. Coating dimensions can therefore be applied predictably. However, hand-spraying is inherently an art and not a science, and experience must be gained by the individual painter to determine the most satisfactory technique for him.

⁶Mr. Harvey Brown, New Jersey Zinc Co. Private communication.

3. Curing

Curing techniques were dictated by the temperature limitation of 300°F (150°C), as stated in the Introduction. Samples were cured by air-drying or by heating at 280°F for 18 hours after a 24-hour air-drying. Curing under controlled atmospheres such as carbon dioxide and water- or carbon dioxide-free air are described later in this section.

A gravimetric study of the air-drying of silicate-bonded zinc oxide revealed that essentially all of the water loss occurred within 1 hour after spraying. Samples heat-cured at 280°F after a 100-hour air-drying displayed an average weight loss of $0.7 \pm 0.1\%$ 24 hours after the heat treatment. Stability and the physical properties investigated indicated that the advantages of a heat cure over air-drying are modest.

4. Summary

In all steps of preparation of materials, adequate precautions should be taken to ensure cleanliness and freedom from contamination. The presence of impurities can greatly affect the stability of paints to a solar-space environment. Detailed information appears later in this report.

B. Determination of Physical Properties

1. Density

A study of weight versus thickness in potassium silicate coatings pigmented with calcined SP 500 (PBR = 4.30) showed the density to be 2.10 ± 0.2 g/cc. Based on a theoretical density of 5.23 g/cc, the porosity of the average coating is about 60%. Such a high void content probably increases reflectance, yielding lower solar absorptance, but the soiling tendency is also heightened. The weight of a 5-mil coating should be approximately 0.170 g/square inch.

2. Thermal Shock

Initial thermal-shock tests for the various paints involved elaborate methods for monitoring temperature and mounting samples in order to meet the requirements of the contract; i.e., the coating must withstand a change of 50°F per minute between 200 and -100°F. A simpler method was devised for more rapid testing of the majority of samples. It consisted of dropping the coating specimen directly into liquid nitrogen contained in a Dewar flask. Cessation of bubbling in about 20 seconds indicated that the specimen had cooled to -320°F. The sample was then removed and placed in an oven at 200°F.

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a temperature which the sample attained in about 4 minutes. Since most materials passed this more severe test, the programmed temperature cycling was not required. The severity as well as the simplicity of this test rendered it adequate for determining thermal-shock resistance

All silicate-bonded zinc oxide coatings of 6 mils or less and also some thin zirconia coatings successfully withstood 10 cycles of the thermal-shock test. No damage to any of the silicate-bonded paints was evident after immersion in liquid nitrogen and removal to room temperature. However, the heating cycle to 200°F cracked some of the thicker coatings. Experimentation showed that thick paints which had not been cooled initially also cracked when heated. When the coated sample is rapidly cooled, the coating undergoes compression, and when heated, tensile strains prevail. For brittle ceramic materials such as the silicate coatings, the compressive strength is about ten times the tensile. This may explain the stability to a decrease and not to an increase, since the aluminum substrates used have a higher thermal expansion than the ceramic coatings

3. Torsion

The torsion apparatus illustrated in Figure 23 was used to study adhesion of paints to substrates. One end of a 1- x 3-inch sample was held rigid while the other end was rotated through the longitudinal axis at a speed of approximately 1° per second. Shear failure in torsion usually occurred with initial separation from the substrates at points A and B (see Figure 24). Subsequent failure along the dotted diagonal line resulted almost immediately, except in a few cases. It is possible that the grips holding the sample in place at the ends may contribute additional stress which would not exist in pure torsion. The condition of loading in pure torsion implies that the end sections of the bar are free to warp, since there are no constraining forces to hold them in their respective planes.⁷ Thus the angle-at-failure reported for various samples in torsion may actually be lower than the true value.

Torsional stress resistance as a function of thickness in silicate-bonded zinc oxide coatings is illustrated graphically in Figure 25. The results for Series 1, 2, and 3 indicate that thermal shock had no deleterious effect on adhesion. No significant difference in angle-at-failure was evident for heat-cured versus air-dried samples (Series 1

⁷Roark, R. J., "Formulas for Stress and Strain" McGraw-Hill Book Co., 1954.

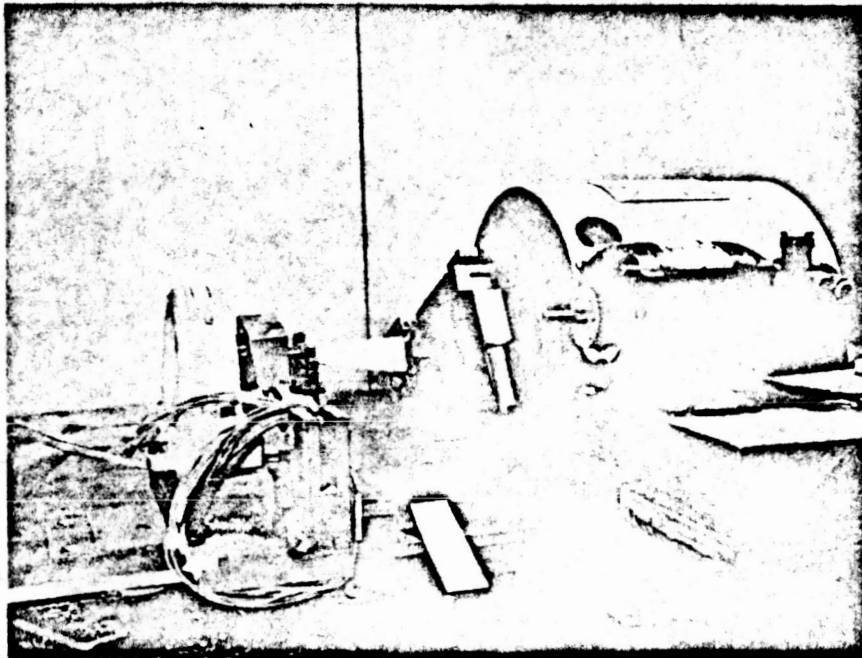


Figure 23

TORSION TEST APPARATUS

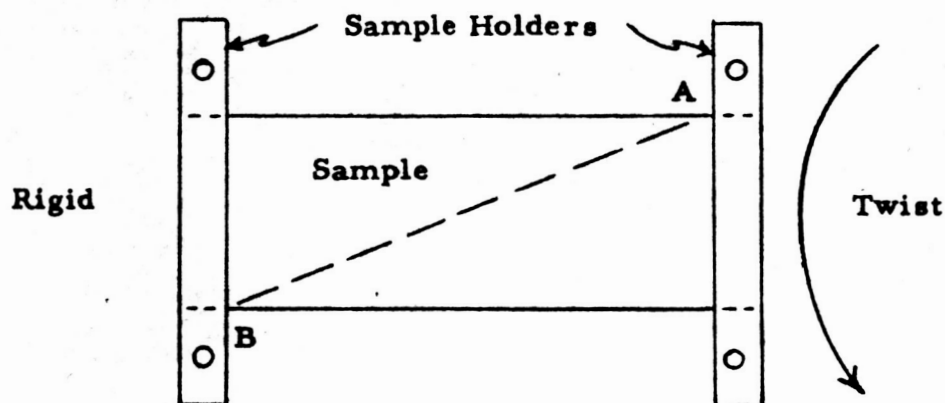


Figure 24

TORSIONAL FAILURE

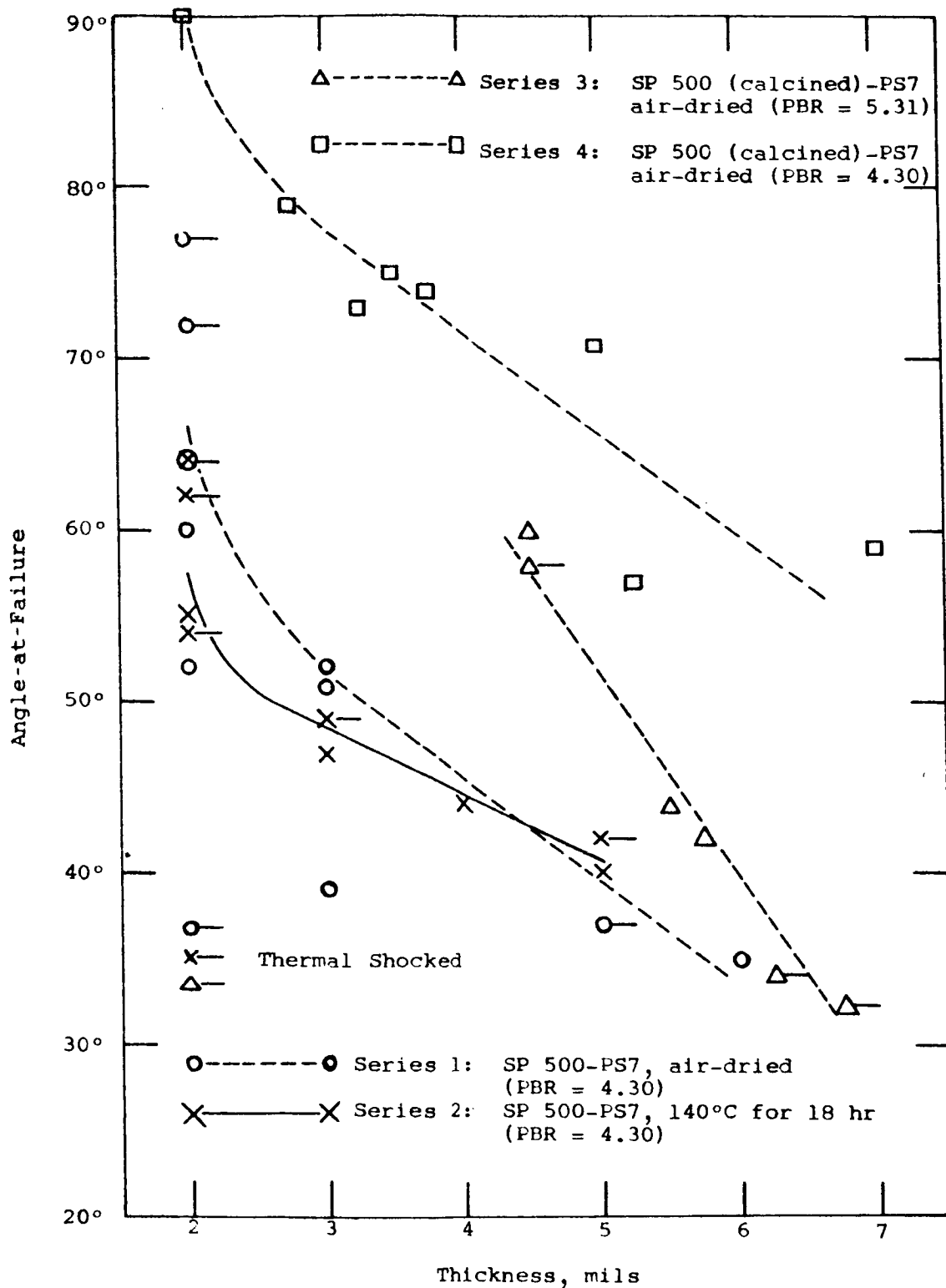


Figure 25

TORSION VERSUS THICKNESS IN ZINC OXIDE-PS7 COATINGS

and 2). The values for coatings pigmented with zinc oxides such as AZO-55LO, E-P 730, E-P 414, and XX 254 were similar to those for SP 500-pigmented paints. Series 3 represents samples of a higher PBR, 5.31, prepared fairly recently. Coatings of the most recent vintage are shown as Series 4. As Figure 25 reveals, the curve for this last series is displaced upward, indicating improved torsional stress resistance. This improvement in physical properties is attributed to refinements in spraying technique.

Torsional stress resistance of all silicate-bonded zinc oxide coatings appears to be primarily a function of thickness. As in the thermal-shock tests, the samples all survived a stress condition much more severe than that expected in actual practice.

4. Fatigue

A test method which may more closely simulate actual launch and flight conditions consists of subjecting a sample first to fatigue and then to thermal shocking. The fatigue machine rapidly vibrated one end of a 1- x 3-inch coated specimen while the other end was held rigid. The distance of travel of the free end (0.01 inch) was determined from the formula for end-loading of a cantilever:

$$d = \frac{P L^3}{3 E I}$$

where P is load, L is length, E is modulus of elasticity, and I is moment of inertia. The use of a strain value of 1500×10^{-6} inches/inch (75% of the yield strength of aluminum) in the calculation precluded plastic deformation of the aluminum.

Various samples were subjected to over 10,000 cycles in a 6-minute period (1725 cycles/minute). They were then thermally shocked for 10 cycles by immersion in liquid nitrogen followed by rapid heating to 200°F. None of the zinc oxide-silicate specimens were visibly affected by this combination of physical and thermal stresses.

5. Abrasion

The abrasion resistance of paints incorporating various zinc oxides was tested with a Taber Abraser. Results showed that hardness of SP 500 coatings was improved by precalcination of the pigment, by decreasing the PBR, or by heat curing. Although zinc oxide coatings are relatively soft, this very softness may be advantageous because stripping by abrasion would not be difficult should repainting be necessary.

6.3-5.5 22

One of the many capabilities which the thermal-control paints must possess is the ability to take the shearing stresses of mechanical fastening (e.g., bolts, screws, etc.). A 1- x 3-inch aluminum panel with two 1/4-inch holes was painted with a calcined SP 500 zinc oxide-PS7 potassium silicate paint. After a 3-day air cure, bolts were screwed tightly to the painted surface, and the nuts were placed on the opposite side. Releasing of the bolts did not crack or chip the coating, as observed under 10x magnification. The softness of the coating permitted the bolt head to grind into the surfaces; this compaction, plus some transfer of metal from the bolt to the coating, were the only effects observed.

6. Effect of Substrate Material

Spacecraft thermal control may require coatings for surfaces other than aluminum, such as polished gold, Dow #7 conversion-coated magnesium, and fiber glass. Satisfactory adhesion on 6061 T6 aluminum was achieved by abrading the metal with #60 Aloxite cloth. Abrasion of gold with #240 paper and fiber glass with #60 cloth resulted in limited adhesion on the former and good adhesion on the latter with a calcined SP 500-potassium silicate paint. Dow #7 required no surface preparation other than washing for satisfactory adhesion. Buildup of a coating in excess of 4 mils on abraded gold resulted in cracked, nonadherent films. Although cracking sometimes occurred in coatings over 7 mils thick on aluminum, the coating still adhered to the substrate.

Samples of coatings applied to the various substrates, with the exception of gold, were subjected to fatigue, thermal shock, and torsion. No significant effect due to substrate material was revealed. Resistance to these physical stresses of coatings applied on Dow #7 and on fiber glass was equally as good as coatings applied on aluminum.

7. Summary

The various physical tests indicate that with proper care in application, satisfactory properties can be expected from zinc oxide-silicate coatings on aluminum, Dow #7, and fiber glass. Although these properties can be optimized by using thinner coatings, optical requirements demand coatings of at least 4 mils. It is recommended that coatings in excess of 6 mils be avoided to preclude possible cracking and significant losses in mechanical properties.

C. Determination of Optical Properties

1. Effect of Coating Thickness

Studies were conducted to determine the effect of coating thickness on solar absorptance and emittance. Figure 26 graphically illustrates the solar absorptances of SP 500 zinc oxide-PS7 potassium silicate coatings which had a PBR of 4.30 and a solids content of 46.3%. The data reveal that minimum solar absorptance was obtained with a coating thickness of about 5 mils. Approximately the same thickness was necessary for minimum solar absorptance of coatings pigmented with calcined SP 500 (Figure 27). The randomness of points in Figures 26 and 27 can be attributed to slight variations in the hand-spraying technique, which could introduce minor dissimilarities in surface pigment concentration, porosity, and other factors. Another possible source of error is micrometer measurement of thickness.

Figures 26 and 27 show that minimal solar absorptance is approached at a thickness of 4 mils. The predictability of the solar absorptance of a coating thicker than 4 mils is ± 0.01 . For satisfactory physical properties, coatings of 6 mils or less are desirable. The working range therefore should be between 4 and 6 mils, which can be readily obtained by a sprayer after some experimentation. Spectral solar absorptance curves for coatings of various thicknesses are presented in Figure 28.

Total normal emittance is relatively insensitive to coating thickness. Ten samples which range from 1 to 5 mils exhibited emittance values of 0.94 to 0.98. Thus the deciding criteria for thickness requirements is the solar absorptance desired.

2. Effect of Zinc Oxide Calcination

Zinc oxide powders were calcined at various temperatures to determine what heat treatment would yield a material of improved physical properties with the same optical properties as those of the uncalcined powder. The reflectances of paints incorporating calcined SP 500 show that temperatures higher than 750°C produced a permanent color change (see Table 11). On this basis, 700°C was determined as a suitable calcination temperature for SP 500 zinc oxide.

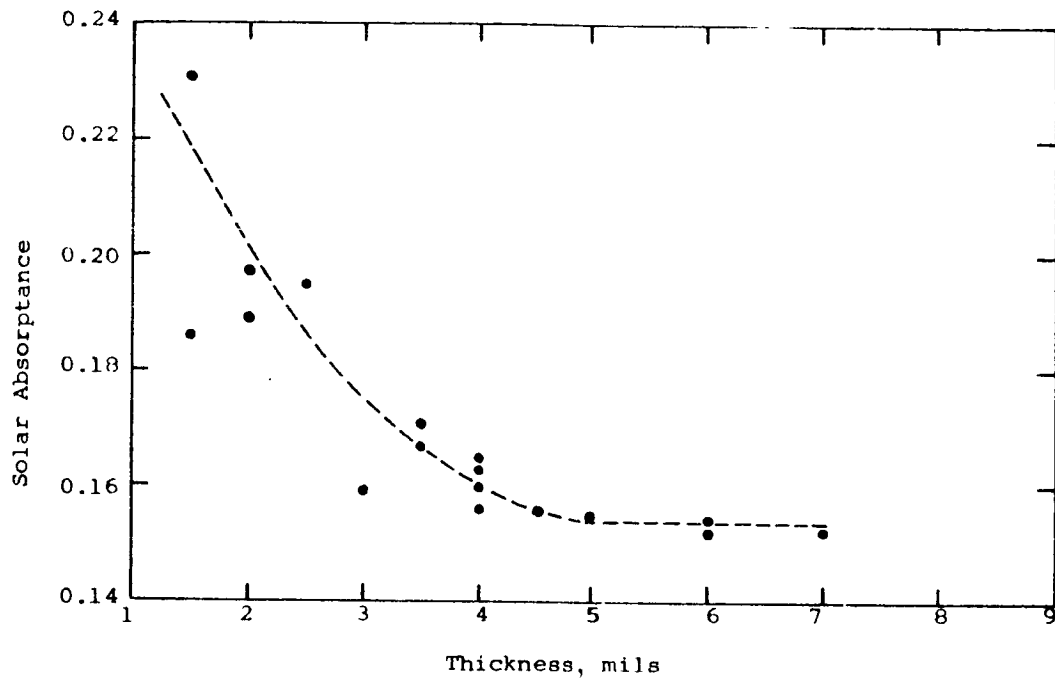


Figure 26

SOLAR ABSORPTANCE VERSUS THICKNESS IN ZINC OXIDE (CALCINED) COATINGS

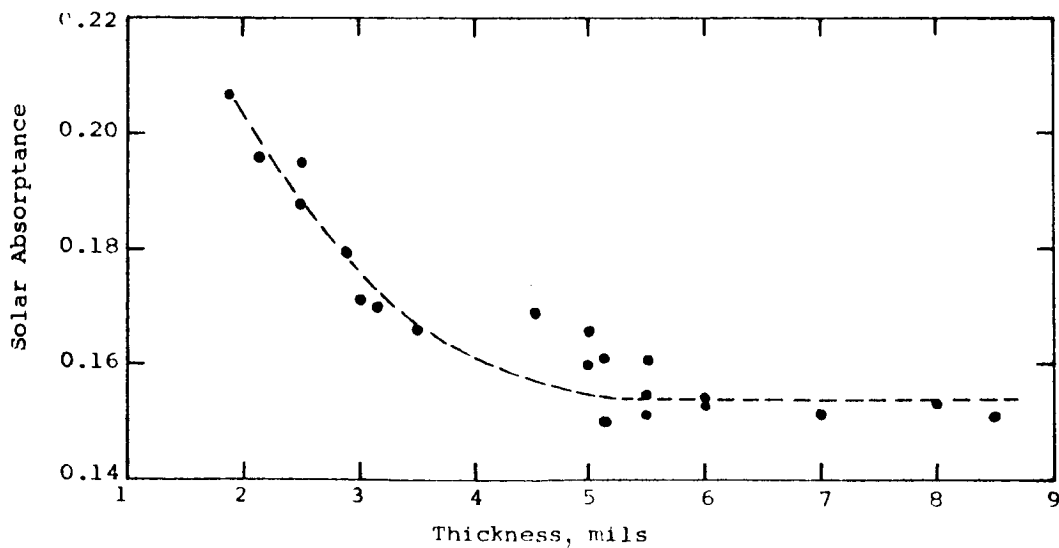


Figure 27

SOLAR ABSORPTANCE VERSUS THICKNESS
IN ZINC OXIDE (CALCINED)-F37 COATINGS

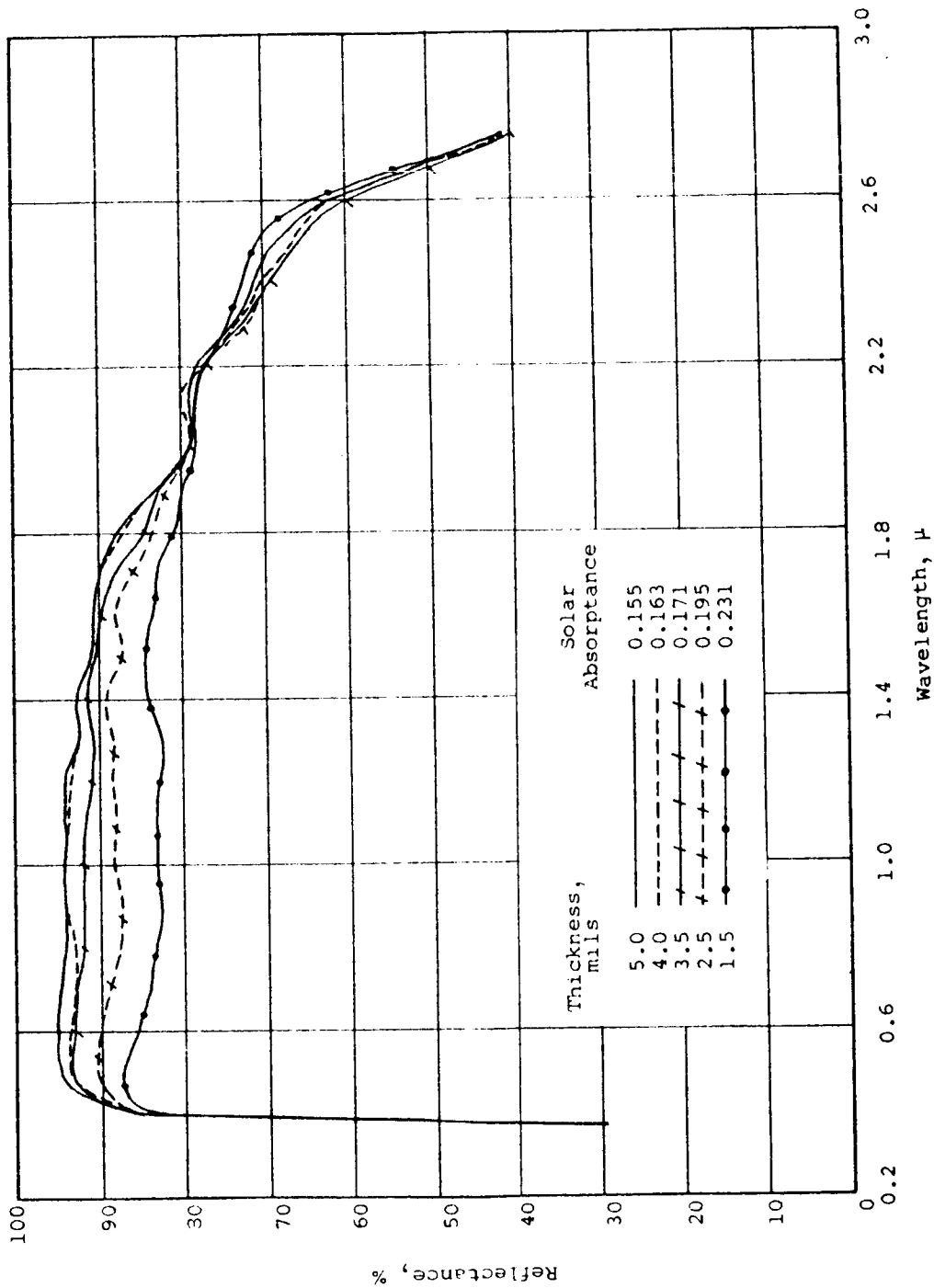


Figure 28
SOLAR SPECTRAL REFLECTANCE CURVES FOR VARIOUS THICKNESSES
OF ZINC OXIDE (CALCINED) -FS7 COATINGS

D. Stability to a Simulated Space Environment

1. Preliminary Studies

In all the early studies zinc oxide paints were clearly more stable than other inorganic coatings. Results of the early tests in the oil-diffusion-pumped system are tabulated in Table 10. Very small reflectance losses, mainly in the 440-m μ region of the visible spectrum were experienced by all the coatings.

Various effects were investigated in these short-term preliminary runs. The use of different alkali silicate binders or grades of zinc oxide (Z13 through Z20) did not affect stability. Lowering of the PBR to 2.13 (Z9) did not affect degradation. The strong increase in initial solar absorptance, however, suggested the use of a higher PBR. The stability of paints applied by brush-painting (Z3 and Z8) was comparable to that of sprayed coatings. Use of an overlayer of PS7 vehicle, intended as a washable coating (Z22), was not detrimental to stability. Physical failure of this topcoat after washing, however, precluded further study of this composite coating.

Total normal emittance values were determined for some of the coatings before and after space simulation. The high values, all in excess of 0.90, were virtually unaffected.

2. Effect of Soiling and Cleaning

A number of silicate-bonded zinc oxide coatings were deliberately soiled by immersion in Duo Seal vacuum-pump oil. This simulates one of the soiling problems which can be expected to occur in satellite evaluation tests. After removal from the oil, the samples were exposed to ambient conditions for 5 hours. The excess oil was then removed with paper towelling. Two cleaning operations followed, the first consisting of wiping with acetone-soaked paper towels and the second consisting of washing with Alconox-tap water and scouring with a nylon brush. Final rinsing with distilled water preceded drying under an airblast and complete drying at 130°C. Moderate care in all the operations prevented any apparent damage to the coatings. The samples were exposed to ultraviolet irradiation in the oil-diffusion-pumped vacuum system.

As shown in Table 11, a slight decrease in reflectance resulted for most of the soiled and cleaned (S-W) samples. Exceptions to this were some samples of initial reflectance lower than 80% at 440 m μ ; these coatings exhibited a slight increase in reflectance. Upon exposure to the simulated space environment many of the samples which suffered losses on

Table 10

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS
All samples cured at 140°C for 18 hr.

| Sample | Composition | | | Solids Content, % | Remarks | Exposure | | Reflectance, % | | Solar Absorbance | | Emittance, ϵ |
|--------|-------------|--------|------|-------------------|--|----------|--------------|----------------|--------------|----------------------|----------------------|-----------------------|
| | Pigment | Binder | PBR | | | ESH | Solar Factor | 440 m μ | 600 m μ | $\frac{a}{\Delta a}$ | $\frac{a}{\Delta a}$ | |
| Z1 | SP 500 | PS7 | 4.30 | 46.3 | | 0 75 | 1.5 | 96.0 95.5 | 98.0 98.0 | | | |
| Z2 | SP 500 | PS7 | 4.30 | 46.3 | | 0 200 | 3 | 95.0 92.5 | 97.5 96.5 | .149 .156 | .007 | |
| Z3 | SP 500 | PS7 | 4.30 | 56.9 | Brush-painted | 0 200 | 3 | 94.0 91.5 | 96.5 95.5 | .164 .177 | .013 | |
| Z4 | SP 500 | PS7 | 2.13 | 51.9 | | 0 200 | 3 | 87.5 84.5 | 86.5 85.5 | | | |
| Z5 | SP 500 | PS7 | 4.30 | 46.3 | | 0 200 | 3 | 96.0 93.5 | 98.5 97.5 | .132 .138 | .006 | .98 .99 |
| Z6 | SP 500 | PS7 | 4.30 | 46.3 | Applied on organic Leonite-TiO ₂ primer | 0 200 | 3 | 95.5 93.5 | 98.5 98.0 | .133 .139 | .006 | .98 .99 |
| Z7 | SP 500 | PS7 | 4.30 | 46.3 | | 0 200 | 3 | 92.5 89.5 | 98.5 97.5 | .131 .136 | .005 | .93 .95 |
| Z8 | SP 500 | PS7 | 4.30 | 56.9 | Brush-painted | 0 200 | 3 | 94.5 90.5 | 98.0 96.0 | .146 .150 | .004 | |
| Z9 | SP 500 | PS7 | 2.13 | 51.9 | | 0 200 | 3 | 88.5 86.5 | 89.5 88.5 | .258 .269 | .011 | .93 .95 |
| Z10 | SP 500 | PS7 | 4.30 | 46.3 | | 0 300 | 3 | 94.0 93.0 | 97.0 98.0 | .139 .142 | .003 | |

| | | | | | | | | | | | |
|-----|------------------------|------------|------|--------|--|----------|-----|--------------|--------------|--------------|------|
| Z11 | SP 500 | PS7 | 4.30 | 52.9 | Formulation contained 1 drop organic wetter | 0 300 | 3 | 93.0 91.5 | 97.5 97.0 | .143 .161 | .018 |
| Z12 | SP 500 | PS7 | 4.30 | 52.9 | Formulation contained 1 drop organic wetter. Applied on organic Leonite-ZnO primer. | 0 300 | 3 | 93.5 92.5 | 97.5 97.5 | .144 .152 | .008 |
| Z13 | SP 500 | Kasil 1 | 5.45 | ca. 45 | | 0 300 | 3 | 92.0 91.0 | 97.0 96.5 | .146 .154 | .008 |
| Z14 | SP 500 | S-J5 | 4.72 | ca. 45 | | 0 300 | 3 | 91.5 91.5 | 96.5 96.5 | .150 .154 | .004 |
| Z15 | SP 500 | N-silicate | 3.88 | ca.45 | | 0 300 | 3 | 89.5 90.5 | 96.5 96.5 | .152 .157 | .005 |
| Z16 | AZO-66 | PS7 | 4.30 | 46.3 | | 0 300 | 3 | 93.5 92.0 | 96.5 96.5 | .154 .165 | .011 |
| Z17 | AZO-55LO | PS7 | 4.30 | 56.9 | | 0 300 | 3 | 85.0 85.0 | 94.5 93.0 | - .192 | |
| Z18 | USP | PS7 | 4.30 | 46.3 | | 0 300 | 3 | 94.5 92.0 | 96.0 96.0 | .161 .170 | .009 |
| Z19 | AZO-55LO | PS7 | 4.30 | 56.9 | | 0 250 | 2.5 | 81.5 80.0 | 92.0 91.5 | | |
| Z20 | XX 504 | PS7 | 4.30 | 61.7 | | 0 250 | 2.5 | 78.5 76.0 | 88.5 87.5 | | |
| Z21 | SP 500 | PS7 | 2.87 | 49.2 | | 0 250 | 2.5 | 84.0 82.0 | 88.0 87.5 | | |
| Z22 | SP 500 | PS7 | 4.30 | 46.3 | Sprayed with an overlay of PS7 | 0 250 | 2.5 | 88.5 87.0 | 95.0 95.0 | | |
| Z23 | 2 E-P 730: 1 SP 500 | PS7 | 4.30 | 61.7 | | 0 270 | 3 | 73.5 72.5 | 86.5 86.5 | | |

Table 11

COMBINED EFFECTS OF SOILING AND WASHING AND OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS
All samples cured at 140°C for 18 hr.

| Sample | Pigment | Composition* | | Solids Content, % | Exposure | | Reflectance, % | |
|--------|----------|------------------------|------|----------------------|-------------------|-----------------|----------------------|----------------------|
| | | Pigment Calcination | PBR | | ESH | Solar Factor | 440 mμ | 600 mμ |
| Z24 | SP 500 | | 4.30 | 46.3 | 0 250 | 2.5 | 90.5 90.0 | 92.5 94.0 |
| Z25 | AZO-55LO | | 4.30 | 56.9 | 0 250 | 2.5 | 82.5 81.0 | 92.0 93.0 |
| Z26 | XX 504 | | 4.30 | 60.4 | 0 250 | 2.5 | 77.5 75.5 | 88.0 88.5 |
| Z27 | SP 500 | | 4.30 | 46.3 | 0 S-W** 225 | 2.5 | 91.0 90.5 90.5 | 94.5 92.5 94.0 |
| Z28 | SP 500 | | 3.58 | 49.3 | 0 S-W 270 | 3 | 89.0 88.5 87.0 | 93.5 90.5 92.0 |
| Z29 | SP 500 | | 3.22 | 51.3 | 0 S-W 225 | 2.5 | 89.5 86.0 86.5 | 92.5 88.5 91.0 |
| Z30 | SP 500 | 66 hr at 500°C | 4.30 | 52.9 | 0 S-W 225 | 2.5 | 93.0 91.5 91.0 | 97.5 95.5 96.0 |
| Z31 | SP 500 | 18 hr at 650°C | 4.30 | 56.9 | 0 S-W 270 | 3 | 94.0 90.5 89.0 | 97.0 94.5 95.0 |
| Z32 | SP 500 | 2 hr at 700°C | 4.30 | 52.9 | 0 S-W 225 | 2.5 | 91.0 88.5 89.0 | 94.5 91.0 93.0 |
| Z33 | SP 500 | 16 hr at 700°C | 4.30 | 56.9 | 0 S-W 225 | 2.5 | 93.5 90.5 90.5 | 97.5 95.0 95.5 |

| | | | | | | | |
|-----|----------|----------------|------|------|-------------------|----------------------|----------------------|
| Z34 | SP 500 | 2 hr at 750°C | 4.30 | 56.9 | 0 S-W 270 | 89.0 87.0 85.5 | 95.5 93.5 94.0 |
| | | | | | 3 | | |
| Z35 | SP 500 | 12 hr at 800°C | 4.30 | 64.4 | 0 S-W 225 | 54.0 57.5 56.0 | 75.0 77.0 76.5 |
| | | | | | 2.5 | | |
| Z36 | SP 500 | 1 hr at 1000°C | 4.30 | 64.4 | 0 S-W 225 | 76.0 75.5 75.0 | 83.0 80.5 83.0 |
| | | | | | 2.5 | | |
| Z37 | AZO-55LO | | 3.22 | 59.0 | 0 0 S-W 225 | 77.0 77.5 75.0 | 87.0 86.5 85.5 |
| | | | | | 2.5 | | |
| Z38 | AZO-55LO | 16 hr at 700°C | 4.30 | 61.7 | 0 S-W 225 | 87.5 87.5 86.5 | 94.5 93.5 93.0 |
| | | | | | 2.5 | | |
| Z39 | E-P 730 | | 4.30 | 73.0 | 0 S-W 270 | 52.5 56.5 55.0 | 75.0 76.5 76.5 |
| | | | | | 3 | | |
| Z40 | E-P 414 | | 4.30 | 56.9 | 0 S-W 270 | 79.0 80.0 76.5 | 91.5 88.5 88.5 |
| | | | | | 3 | | |
| Z41 | XX 254 | | 4.30 | 61.7 | 0 S-W 270 | 78.5 78.5 76.0 | 89.5 87.5 87.0 |
| | | | | | 3 | | |
| Z42 | XX 254 | | 4.30 | 73.0 | 0 S-W 270 | 75.5 78.0 75.0 | 89.0 88.5 87.0 |
| | | | | | 3 | | |

* The binder for all coatings was PS7.

** S-W: After soiling and washing.

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washing bleached slightly. On the other hand, coatings which showed an increased reflectance on washing revealed slight losses after exposure to the simulated space environment. In all cases the washing appeared to have adequately removed any degradable residual oil.

3. Long-Term Tests

The longer-term tests were conducted in the ion-pumped vacuum system with an externally mounted ultraviolet lamp. Exposures of 450 to 4170 ESH at solar factors ranging from 8 to 18 suns were used. The limited capacity of the water-cooled shelf in the chamber dictated sample geometries of 1 inch square for maximum use.

Preliminary Tests. More significant optical changes in the zinc oxide compositions became apparent in the longer tests. The data tabulated in Table 12 reveal the effects of different zinc oxides, pigment calcination, lower PBR, and air cure versus heat cure.

The SP 500 and AZO-55LO coatings were slightly more stable than paints pigmented with E-P 414 or XX 254. The lower solar absorptances and ease of obtaining good coatings were additional reasons for concentrating effort on the first two materials. An SP 500 paint (Z50) of larger particle size, 2.1 μ , exhibited good stability. However, the high solar absorptance and also possible difficulties in obtaining larger batches of this experimental powder were negative factors.

Pigment calcination did not influence the degradation of SP 500 paints (Z43 through Z46) but was deleterious to AZO-55LO (Z51 through Z54). The pigment studies described in Section IV, however, indicated that calcination was beneficial.

Lowering of the PBR was detrimental to initial solar absorptance and also to stability (Z45 and Z46 versus Z47). The improved physical properties realized with more binder were more than offset by decreased stability.

The results for Z48 versus Z49 and Z53 versus Z54 revealed no significant gain in stability by curing at 280°F for 18 hours rather than air-drying. Elimination of a heat cure in actual practice would be desirable and, from the results of physical tests as well as the space-simulation studies, appears feasible.

Miscellaneous Physical Effects. A number of samples were subjected to various physical treatments prior to stability tests. Optical changes in these paints are tabulated in Table 13.

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Considerable degradation occurred in Z58. Obviously application of a topcoat over a soiled area was not sufficient to retain stability. It is possible that cleaning might remove any soluble degradable material which may be dissolving in the second coat during respraying. Physical punishment prior to ultraviolet irradiation in vacuum had no significant influence on stability (Z59).

Spraying techniques were varied for samples Z60 and Z61. It was anticipated that "wet" spraying would permit greater settling of the pigment than the "dry" method and would therefore result in a vehicle-rich surface which would be more degradable. However, the results were the reverse of what was expected. Good stability was exhibited by both samples in this long test.

An experiment was conducted to determine the effect of possible milling impurities. Comparisons between Z62 and Z65 and between Z63 and Z66 indicate that ball-milling for 6 to 8 hours did not introduce enough foreign materials to influence stability.

A definite source of discoloration was residue from acetone. Distinct yellow streaks were evident on the edges of Z64, which had been "cleaned" with acetone. The degradation is only partially reflected in the optical measurement, since the reflectometer was geared to a 1-inch diameter and viewed mainly the center of the sample.

Sample Z67 was formulated by using PS7 from a batch opened one year previously. Except for tapping of small amounts about once a week, the container was kept tightly covered during that time. Sample Z68 was made from a freshly opened supply of PS7. As shown in Table 13, no effect due to the different binder batches was evident and both coatings had excellent stability.

Table 12

COMBINED EFFECTS OF USING DIFFERENT GRADES OF ZINC OXIDE AND OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS

| Sample | Cure | Test No. | Composition * | | | | Solids Content, % | Exposure | | Reflectance, % | | Solar Absorbance | |
|--------|-----------------|----------|---------------|---------------------|------|--|-------------------|-----------|--------------|----------------|--------------|------------------|-----------------------------|
| | | | Pigment | Pigment Calcination | PBR | | | ESH | Solar Factor | 440 mμ | 600 mμ | $\frac{A}{a}$ | $\frac{\Delta A}{\Delta a}$ |
| Z43 | 140°C for 13 hr | 1 | SP 500 | | 4.30 | | 46.3 | 0 450 | 0 10 | 89.0 92.5 | 95.5 95.5 | | |
| Z44 | 140°C for 18 hr | 1 | SP 500 | 2 hr at 750°C | 4.30 | | 64.4 | 0 450 | 0 10 | 87.0 87.0 | 95.5 95.5 | | |
| Z45 | 140°C for 18 hr | 2 | SP 500 | | 4.30 | | 46.3 | 0 2100 | 0 10 | 93.5 87.5 | 97.5 94.5 | | |
| Z46 | 140°C for 18 hr | 2 | SP 500 | 16 hr at 700°C | 4.30 | | 56.9 | 0 2100 | 0 10 | 93.5 87.0 | 96.0 93.0 | | |
| Z47 | 140°C for 18 hr | 2 | SP 500 | | 3.22 | | 51.3 | 0 2100 | 0 10 | 99.0 80.5 | 93.5 87.5 | | |
| Z48 | 140°C for 18 hr | 3 | SP 500 | | 4.30 | | 46.3 | 0 1700 | 0 8.7 | 93.5 85.0 | 95.5 91.5 | .173 .195 | .022 |
| Z49 | Air-dried | 3 | SP 500 | | 4.30 | | 46.3 | 0 1700 | 0 8.7 | 92.5 85.0 | 95.0 91.5 | .172 .197 | .025 |

| | | | | | | | | | | | |
|------|-----------------|----|----------------------------|----------------|------|---|------|--------------|--------------|--------------|------|
| Z50 | 140°C for 18 hr | 9 | SP 500, 2.1-μ particles | 4.30 | 73.0 | 0 | 10.7 | 63.0 59.5 | 79.0 73.0 | .336 .358 | .022 |
| Z51, | 140°C for 18 hr | 3 | AZO-55LO | 4.30 | 56.9 | 0 | 8.7 | 84.5 79.0 | 93.0 90.0 | .202 .217 | .015 |
| Z52 | 140°C for 18 hr | 3 | AZO-55LO | 16 hr at 700°C | 56.9 | 0 | 8.7 | 88.5 78.5 | 94.0 89.0 | .180 .205 | .025 |
| Z53 | 140°C for 18 hr | 9 | AZO-55LO | 16 hr at 700°C | 56.9 | 0 | 10.7 | 90.0 81.5 | 94.5 90.0 | .165 .193 | .028 |
| Z54 | Air-dried | 21 | AZO-55LO | 16 hr at 700°C | 56.9 | 0 | 9.5 | 90.0 82.5 | 95.5 91.0 | .169 .193 | .024 |
| Z55 | 140°C for 18 hr | 3 | E-P 414 | 4.30 | 56.9 | 0 | 8.7 | 83.5 73.5 | 91.5 85.5 | .210 .240 | .030 |
| Z56 | 140°C for 18 hr | 4 | E-P 414 | 16 hr at 700°C | 61.7 | 0 | 10 | 85.5 81.5 | 93.0 89.5 | | |
| Z57 | 140°C for 18 hr | 3 | XX 254 | 4.30 | 61.7 | 0 | 8.7 | 82.5 70.5 | 90.5 84.5 | .217 .249 | .032 |

* The binder for all coatings was PS7.

Table 13

COMBINED EFFECTS OF MISCELLANEOUS TREATMENTS AND OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS

| Sample | Cure | Test No. | Composition* | | Treatment | Exposure | | Reflectance, % | | Solar Absorbance | |
|--------|-----------------|----------|-----------------------|-------------------|---|-----------|--------------|----------------|--------------|------------------|-----------------------------------|
| | | | Pigment Calci- nation | Solids Content, % | | ESH | Solar Factor | 440 mμ | 600 mμ | $\frac{a}{d}$ | $\frac{\Delta a}{\Delta \lambda}$ |
| Z58 | Air-dried | 4 | | 46.3 | Initial coat soiled with dirt, then coated with same composition 3-1/2 mils thick. No attempt was made to clean the first coat. | 0 1200 | 10 | 91.5 63.5 | 96.5 81.0 | | |
| Z59 | Air-dried | 4 | | 46.3 | Sample was fatigued and thermally shocked. | 0 1200 | 10 | 88.0 86.0 | 94.5 90.5 | | |
| Z60 | 140°C for 18 hr | 5 | | 46.3 | Sample sprayed "wet" (heavy application), so glossiness was evident throughout the procedure. | 0 3100 | 10 | 94.0 86.0 | 97.0 93.0 | .172 .184 | .012 |
| Z61 | 140°C for 18 hr | 5 | | 46.3 | Sample sprayed "dry" (lighter and slower application), so glossiness was a signal for temporary cessation of painting. | 0 3100 | 10 | 93.5 84.5 | 95.0 91.0 | .187 .207 | .020 |
| Z62 | Air-dried | 7 | | 46.3 | Formulation was ball-milled for only 1/2 hr. | 0 3350 | 17.6 | 96.0 91.0 | 96.0 93.5 | .156 .170 | .014 |
| Z63 | Air-dried | 9 | | 46.3 | Formulation was mixed by agitation for 1 hr; no balls were used. | 0 1700 | 10.7 | 95.5 90.5 | 96.5 94.0 | .148 .167 | .019 |
| Z64 | Air-dried | 7 | 16 hr at 700°C | 56.9 | Edges of sample wiped with reagent-grade acetone and air-dried. | 0 3350 | 17.6 | 96.0 86.5 | 96.0 92.0 | .144 .174 | .030 |
| Z65 | Air-dried | 7 | 16 hr at 700°C | 56.9 | Formulation was ball-milled for 6 hr. | 0 3350 | 17.6 | 91.0 85.5 | 89.5 87.5 | .205 .216 | .011 |
| Z66 | 140°C for 18 hr | 9 | | 46.3 | Formulation was ball-milled for 8 hr. | 0 1700 | 10.7 | 94.5 87.0 | 95.5 92.0 | .164 .181 | .017 |
| Z67 | Air-dried | 18 | 16 hr at 700°C | 46.3 | The binder was from a 1-yr-old batch. | 0 1600 | 10.2 | | | .175 .183 | .008 |
| Z68 | Air-dried | 18 | 16 hr at 700°C | 46.3 | The binder was from a freshly opened batch. | 0 1600 | 10.2 | | | .164 .173 | .009 |

* The pigment was SP 500, the binder was PS7, and the PBR was 4.30 for all samples.

Effects of Curing and Storage. The randomness of some test results suggested the possibility of an effect due to an aging factor. A subsequent test involving two samples, Z77 and Z78, which had been stored for 4 months, revealed severe degradation. Sample Z77 was two-thirds of a 1- x 3-inch panel; the other one-third, Z60 in Table 13, had shown good stability in an earlier test. The data for Z77 and Z78 along with other samples investigated for curing and storage effects appear in Table 14.

Another sample which had been stored for the same length of time was cut into three pieces, each of which received different treatments. The data for these samples, Z79, Z80, and Z81, reveal the beneficial effect of washing and maximization of stability by heating the paint at 500°C. In view of these results, contamination of the paints appears to be possible. Washing extracted some of the degradable component. It is possible that additional washing may have removed even more. The heat treatment was not at a high enough temperature to decompose such materials as potassium carbonate, potassium sulfate, or zinc orthosilicate had they been present as a contributory factor in degradation. It appears that, on storing, the coating collected impurities which had not actually reacted chemically with the paint but instead were held physically in the porous coatings.

Sample Z83 was cured in a carbon dioxide atmosphere by placing it in a closed box with dry ice. The deleterious effect on stability was obvious from the change in absorptance. Poor stability was also exhibited by Z84. A zinc oxide-potassium silicate formulation has a limited, if any, shelf life. Difficulties in remixing and spraying also resulted after storage.

The increase in absorptance for the compositions of higher PBR was large in view of the heat treatment given these samples (Z85 and Z86). It would be logical to assume that a higher PBR should enhance stability. Studies with silicones (Section VIII) corroborated this thesis.

A group of samples (Z87 through Z92) prepared at the same time from the same formulation was irradiated in Test 22. As shown in Table 14, the coatings received various types of cure and storage. Surprisingly, the most stable coating (Z87) was air-cured and stored. Its change in solar absorptance was the smallest noted in any of the extended (>1000 ESH) tests. The desiccator cure appeared to be deleterious to stability, and no difference due to storage in air (Z89), under Saran Wrap (Z90), or in the desiccator (Z88) was observed. The undesirable effect of the desiccator cure was partially eliminated by heat treatment (Z91 and Z92). The slightly detrimental effect of curing in a water-free and carbon dioxide-free atmosphere seems paradoxical. However, good stability was exhibited by all coatings in this group.

COMBINED EFFECTS OF VARYING THE CURING AND STORAGE TIMES AND OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS

| Sample | Cure | Treatment | Test No. | Composition * | | | Exposure Solar Factor | Solar Absorbance | | |
|--------|-----------------|--|----------|----------------------|------|-------------------|-----------------------|------------------|----------------|--------------|
| | | | | Pigment Calci-nation | PBR | Solids Content, % | | a ₁ | a ₂ | Δa |
| Z77 | 140°C for 13 hr | Stored for 4 months between sheets of notepad paper in a manila folder on a laboratory bench. | 16 | | 4.30 | 46.3 | 0 1350 | .100 .172 | .060 .239 | .160 .079 |
| Z78 | Air-dried | Same as Z77. | 16 | 16 hr at 700°C | 4.30 | 56.9 | 0 1850 | .098 .152 | .060 .063 | .158 .214 |
| Z79 | 140°C for 13 hr | A 1 x 3-in. sample stored as described above was cut into three 1-in. squares. Z79 was not treated, Z80 was washed with detergent and water, and Z81 was heated at 500°C for 2 hr. | 18 | 16 hr at 700°C | 4.30 | 56.9 | 0 1600 | .116 .152 | .079 .079 | .195 .231 |
| Z80 | 140°C for 18 hr | | 18 | 16 hr at 700°C | 4.30 | 56.9 | 0 1600 | .112 .135 | .077 .075 | .189 .209 |
| Z81 | 140°C for 18 hr | | 18 | 16 hr at 700°C | 4.30 | 56.9 | 0 1600 | .111 .116 | .077 .077 | .188 .193 |
| Z82 | Air-dried | Stored for 1 month as described for Z77 above. | 21 | 16 hr at 700°C | 4.30 | 56.9 | 0 1780 | .101 .132 | .069 .067 | .170 .198 |
| Z33 | Air-dried | Cured in CO ₂ atmosphere. | 21 | 16 hr at 700°C | 4.30 | 56.9 | 0 1780 | .102 .178 | .073 .084 | .175 .263 |
| Z84 | 140°C for 18 hr | Shelf-life sample. The formulation was originally prepared and milled 4 months previously. Vigorous shaking was required to resuspend the pigment. | 21 | | 4.30 | 46.3 | 0 1780 | .096 .159 | .050 .059 | .146 .219 |

| | | | | | | | | | | | | |
|-----|--------------------|--|----|-------------------|------|------|-----------|-----|--------------|--------------|--------------|------|
| Z85 | 140°C for 18 hr | Heated at 500°C for 12 hr. | 21 | 16 hr at 700°C | 4.78 | 56.3 | 0 1780 | 9.5 | .094 .110 | .057 .061 | .151 .171 | .020 |
| Z86 | 140°C for 18 hr | Heated at 500°C for 12 hr. | 21 | 16 hr at 700°C | 5.31 | 53.7 | 0 1780 | 9.5 | .090 .105 | .052 .056 | .141 .161 | .020 |
| Z87 | Air-dried | Stored between sheets of vellum open to the laboratory environment, for 27 days. | 22 | 16 hr at 700°C | 4.30 | 56.9 | 0 1650 | 9 | .099 .103 | .059 .056 | .157 .159 | .002 |
| Z88 | Air-dried | Cured and stored in a desiccator containing Drierite (a desiccant) and Ascarite (a carbon dioxide absorbant) for 27 days. | 22 | 16 hr at 700°C | 4.30 | 56.9 | 0 1650 | 9 | .099 .115 | .062 .063 | .161 .179 | .018 |
| Z89 | Air-dried | Cured in a desiccator for 22 hr and stored in air for 26 days. | 22 | 16 hr at 700°C | 4.30 | 56.9 | 0 1650 | 9 | .100 .115 | .060 .060 | .161 .175 | .014 |
| Z90 | Air-dried | Cured in a desiccator for 22 hr and stored under Saran Wrap for 26 days. | 22 | 16 hr at 700°C | 4.30 | 56.9 | 0 1650 | 9 | .102 .115 | .063 .064 | .165 .179 | .014 |
| Z91 | 140°C for 18 hr | Cured in a desiccator for 22 hr, heated in air at 500°C for 2 hr, and stored in a desiccator for 25 days. | 22 | 16 hr at 700°C | 4.30 | 56.9 | 0 1650 | 9 | .101 .104 | .060 .061 | .161 .165 | .004 |
| Z92 | 140°C for 18 hr | Cured in a desiccator for 22 hr, heated in air at 500°C for 2 hr, and stored in air for 25 days. | 22 | 16 hr at 700°C | 4.30 | 56.9 | 0 1650 | 9 | .103 .109 | .067 .070 | .171 .179 | .008 |

* The pigment was SP 500 and the binder was PS7 for all samples.

4170 ESH Test (No. 23) The most severe space-simulation test in the program was for 4170 ESH at a solar factor of 10.6 suns, corresponding to nearly 6 months of direct extra-terrestrial ultraviolet irradiation. The optical changes plus short histories of the samples appear in Table 15. Good stability was exhibited by Z93 (Figure 29) and Z94. The comparatively superior behavior of the coating with the high PBR, Z94, indicates the feasibility of increasing pigment concentration. The beneficial effect of a 500°C heat treatment is evidenced by the results for Z96. A limited deleterious effect was imparted by washing.

4. Summary

The best inorganic thermal-control coating investigated was PS7 potassium silicate paint pigmented with SP 500 zinc oxide precalcined at 700°C for 16 hours. The PBR and solids content, both by weight, should be 4.30 and 56.9%, respectively. Various effects on stability to a space environment were studied. Probably the most important factor for maximization of the stability of this system is cleanliness. Contamination, whether it be during formulation, application, curing, or storage, must be avoided. A 500°C heating of the paint is also advantageous. Such a treatment was not permitted in this program, however.

Several treatments were found to have little or no effect on stability. Ball-milling of the paint formulation did not introduce enough impurities to change the degradation characteristics. Careful washing and physical stresses such as fatigue and thermal shock also had negligible effect on the paint. The lack of heat-curing was not detrimental to stability. Storage under Saran Wrap or possibly a similar protective plastic should have no influence on the inherent behavior of the paint to the space environment.

Certain factors were shown to be conducive to solar absorptance changes. Foremost was contamination of the coating, e.g., with sebum or acetone residue. Introduction of impurities in a more subtle fashion, such as settling of airborne contaminants, must also be avoided. If a soiled area is to be repainted, it must first be scrupulously cleaned; merely applying a topcoat was not sufficient to restore stability.

The zinc oxide-silicate formulation has a limited shelf life. A degradable system resulted when the mixture was permitted to stand for any length of time. Apparently a fresh batch of paint should be prepared just prior to application. Another deleterious factor was a carbon dioxide cure. Acceleration of curing in such an atmosphere upset the stability of the system.

Table 15

EFFECT OF 4170 ESH OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS
All samples cured by air drying.

| Sample | Composition * | | Treatment | Exposure | | Solar Absorbance | | |
|--------|------------------------|------|-----------|---|-----------------------|------------------|--|----------------|
| | Pigment Calcination | PRR | | ESH | Solar Factor | α_1 | α_2 | $\Delta\alpha$ |
| Z93 | 16 hr at 700°C | 4.30 | 56.9 | Stored in air, between sheets of vellum, for 37 days. | 0 4170 | 10.6 | .102 .063 .165 .120 .059 .179 | .014 |
| Z94 | 16 hr at 700°C | 5.31 | 58.5 | Stored in air, between sheets of vellum, for 21 days. | 0 4170 | 10.6 | .096 .051 .147 .106 .049 .155 | .008 |
| Z95 | 16 hr at 700°C | 4.30 | 56.9 | Stored in air, between sheets of vellum, for 36 days; washed with detergent and water; air-dried for 1 day. | 0 0-washed 4170 | 10.6 | .100 .061 .161 .098 .049 .147 .122 .050 .172 | -.014 .025 |
| Z96 | 16 hr at 700°C | 4.30 | 56.9 | Stored in air, between sheets of vellum, for 24 days; heated at 500°C for 2 hr; stored in air for 13 days. | 0 0-heated 4170 | 10.6 | .102 .064 .166 .101 .058 .159 .109 .057 .166 | -.007 .007 |

* The pigment was SP 500 and the binder was PS7 for all samples.

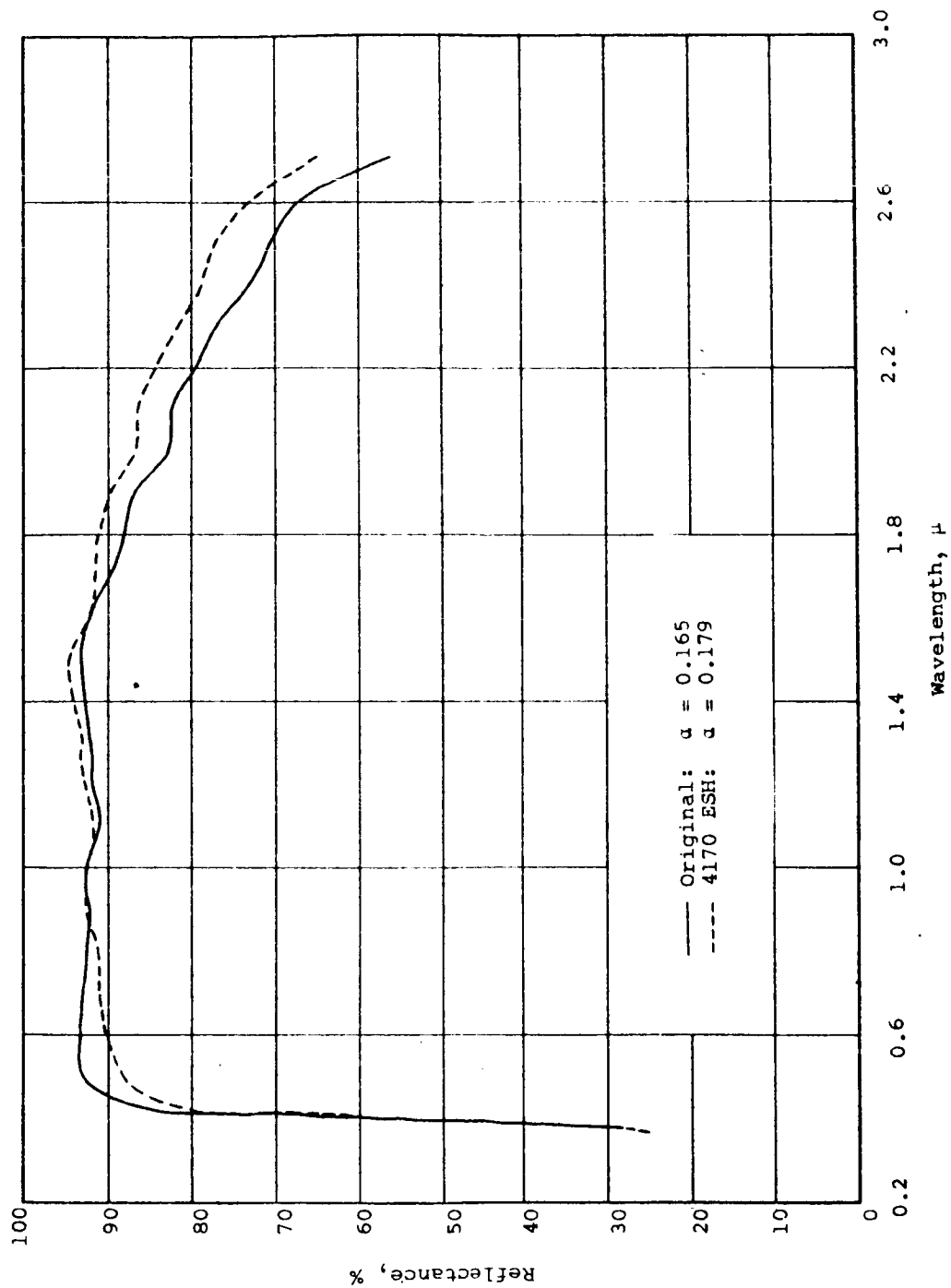


Figure 29
 EFFECT OF 4170 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE
 OF ZINC OXIDE (CALCINED) -F37 COATING (SAMPLE Z93)

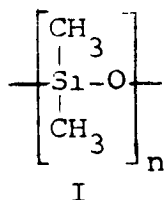
VII. SCREENING OF ORGANIC AND ORGANOMETALLIC PAINTS

A. Preparation of Materials

The organic coating vehicles which were considered can be divided into the following chemical categories: organo-metallic vehicles with organic "framing" groups, fluorine-containing aliphatic resins, organic polyesters, epoxy resins, and miscellaneous vehicles including commercial resins with undisclosed composition. In this discussion, however, these binders are divided into three categories: commercially available silicones, fluorine-containing aliphatic resins, and a modified silicone-epoxy composition. More than 45 resin films were considered for screening. Nearly 300 pigment-binder combinations were prepared, although only about 50 paints were irradiated in vacuum.

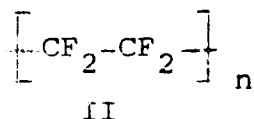
The study of experimental methyl silicone resins comprised a major portion of the non-inorganic phase of the research program. For this reason, the methyl silicone resins which were synthesized during the course of the program are discussed separately in Section VIII.

Four silicones were evaluated: General Electric Company's RTV-11 silicone paste, their LTV-602 silicone potting compound, their SE551-N silicone gum, and Dow Corning Corporation's 806A silicone resin. The first two materials are polydimethylsiloxane polymers with the following generalized structure:

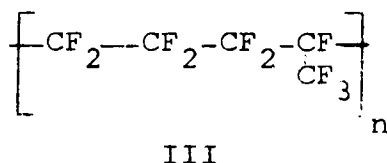


RTV-11 contains silica, calcium oxide, and calcium carbonate as fillers. It is cured with Thermolite 12, a proprietary catalyst obtained from General Electric. LTV-602 is a transparent liquid containing no fillers and is cured by addition of SRC-05 catalyst. Both materials cure at room temperature, but the LTV-602 requires 16 hours unless the temperature is raised to 150 to 200°F. SE551-N is a low-shrink, methyl-phenyl silicone gum stock which is cured with benzoyl peroxide. Dow Corning 806A resin is a methyl-phenyl silicone and possesses a structure which is a cross-linked version of structure I with some of the methyl groups replaced with phenyl groups. This resin requires heating to 480°F to cure, although the addition of a metal soap catalyst or a cross-linking agent such as tetrabutoxy titanium accelerates the cure.

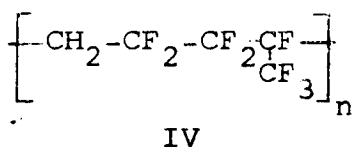
Nine fluorine-containing polymers were evaluated. Those which were obtained from E. I. Du Pont de Nemours and Company were: Teflon TFE Dispersion No. 30, Teflon TFE High Build Clear Finish No. 852-202, Teflon FEP Dispersion No. 120, Viton A, and Viton B. Teflon TFE, or polytetrafluoroethylene, has the structure:



Teflon FEP, a copolymer of tetrafluoroethylene and hexafluoropropylene, has the structure:

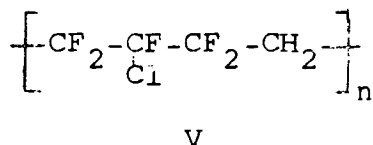


Viton, a copolymer of vinylidene fluoride and hexafluoropropylene, has the structure:



The raw polymer of Viton B gum was dissolved in acetone or methyl ethyl ketone. It required about 10 days before the suspended impurities settled and a clear solution was formed.

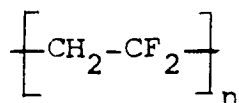
Kel-F resin No. 800 and Kel-F latex No. KF 8213 were obtained from the Minnesota Mining and Manufacturing Company. The resin and latex are each copolymers of vinylidene fluoride and trifluorochloroethylene:



Kel-F No. 8213 was received as an aqueous dispersion. A ketone dispersion was made from it by quenching the aqueous dispersion of the latex with liquid nitrogen, covering the solidified material with acetone, allowing the solid to warm, and decanting the supernatant solution. The process of water extraction was repeated without further freezing. The acetone dispersion was then dried over nonreactive drying agents.

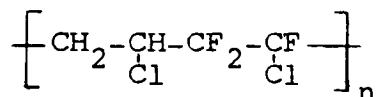
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Kynar No. L-18 was obtained from the Pennsalt Chemicals Corporation and is a polyvinylidene fluoride resin with the structure:



VI

Exon 461 was obtained from the Firestone Plastics Company. It is a copolymer of vinyl chloride and trifluorochloroethylene and has the structure:



VII

The only epoxy resin evaluated was a silicone-epoxy modified acrylic resin known as Leonite 201-S obtained from the Leon Chemical Industries.

B. Paint Formulation

The organic coatings were applied to one surface of an aluminum plate 3 x 1 x 1/16 inches. In this report the paint formulations are designated as P-1, P-2, etc. The designations used in previous reports on this program are listed in Appendix I.

The ratio of pigment to binder in the paint was obtained by dividing the weight of the binder used by the weight of the pigment. The solvents and dispersing agents which were evaporated during the drying and heat-curing treatments were not included in this ratio.

Most of the coatings were prepared by rotating the pigment, the resin, and a solvent in a polyethylene container with glass or silica beads.

C. Stability to a Simulated Space Environment

Only two clear organic polymer films were irradiated: one specimen of Teflon TFE No. 30 and one of RTV-11 silicone. The data for these two coatings appear first in Table 16, which also contains data for other representative organic paints. Comparison of the reflectance changes in P-1 and P-3 illustrates the difference between a phenyl and a methyl silicone binder.

Table 16

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF SEVERAL ORGANIC PAINTS

| Paint No. | Composition | | PBR | Exposure | | Reflectance, % | |
|-----------|--------------------------------|--------------------|------|----------|--------------|----------------|--------------|
| | Pigment | Binder | | ESH | Solar Factor | 440 mμ | 600 mμ |
| - | - | RTV-11 | - | 0 108 | 4 | 73.5 60.5 | 77.5 76.5 |
| - | - | Teflon TFE 30 | - | 0 74 | 4 | 84.7 69.2 | 80.6 74.7 |
| P-1 | SP 500 ZnO | 806A | 0.7 | 0 108 | 4 | 89.0 56.0 | 87.5 83.5 |
| P-2 | SP 500 ZnO | 3E551-N | 3.4 | 0 500 | 4 | 88.5 84.0 | 94.5 93.5 |
| P-3 | SP 500 ZnO | RTV-11 | 1.0 | 0 500 | 4 | 91.0 88.0 | 92.0 91.5 |
| P-4 | SP 500 ZnO | LTV-602 | 5.0 | 0 500 | 4 | 91.0 90.0 | 93.5 93.5 |
| P-5 | ZrO ₂ | Teflon TFE 30 | 0.66 | 0 74 | 4 | 87.8 42.0 | 70.0 59.6 |
| P-6 | Al ₂ O ₃ | Teflon TFE 30 | 0.1 | 0 74 | 4 | 76.6 47.9 | 66.4 58.9 |
| P-7 | SP 500 ZnO | Teflon TFE 852-202 | 0.67 | 0 108 | 4 | 84.0 46.0 | 91.5 74.5 |
| P-8 | SP 500 ZnO | Teflon FEP 120 | 0.4 | 0 314 | 4 | 84.2 52.4 | 77.3 67.5 |
| P-9 | SP 500 ZnO | Viton A | 4.0 | 0 108 | 4 | 88.0 68.0 | 94.0 87.5 |

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| | | | | | | | |
|------|--------------------------------|------------------------------------|------|----------|---|--------------|--------------|
| P-10 | SP 500 ZnO | Viton B | 4.0 | 0 500 | 4 | 88.5 76.5 | 92.0 89.0 |
| P-11 | SP 500 ZnO | Kel-F 800 | 0.5 | 0 108 | 4 | 84.0 64.8 | 77.6 72.7 |
| P-12 | ZnS | Kel-F 800 | 5.0 | 0 108 | 4 | 89.5 49.5 | 92.0 78.0 |
| P-13 | SP 500 ZnO | Kel-F 8213 | 1.5 | 0 108 | 4 | 87.0 52.0 | 87.5 72.5 |
| P-14 | SP 500 ZnO | Kel-F 8213 (acetone dispersion) | 5.0 | 0 500 | 4 | 97.0 80.5 | 98.0 95.0 |
| P-15 | SP 500 ZnO | Kynar L-18 | 5.0 | 0 108 | 4 | 84.0 64.0 | 90.0 81.0 |
| P-16 | ZnS | Exon 461 | 4.0 | 0 108 | 4 | 86.0 39.0 | 89.0 64.5 |
| P-17 | SP 500 ZnO | Exon 461 | 0.5 | 0 108 | 4 | 85.0 10.0 | 80.5 31.5 |
| P-18 | TiO ₂ | Leonite 201-S | 1.25 | 0 74 | 4 | 90.9 85.2 | 92.8 89.2 |
| P-19 | SP 500 ZnO | Leonite 201-S | 0.67 | 0 108 | 4 | 86.0 71.0 | 95.0 83.0 |
| P-20 | MgO | Leonite 201-S | 0.44 | 0 108 | 4 | 93.5 35.0 | 92.5 78.5 |
| P-21 | BN | Leonite 201-S | 0.2 | 0 108 | 4 | 85.0 38.0 | 88.5 75.0 |
| F-22 | Sb ₂ O ₃ | Leonite 201-S | 0.67 | 0 108 | 4 | 85.0 33.0 | 88.0 60.5 |

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although some of the degradation in P-1 at 440 mμ was due to the low PBR. Subsequent silicone paints were formulated at a PBR of about 2.5.

Coating P-4 showed exceptional resistance to degradation; the loss in reflectance at 440 mμ was only 1.0%. The PBR of 5 is much higher than is practical, however. This value is in excess of the critical pigment volume concentration for this pigment-binder combination. The critical pigment volume concentration is reached when there is insufficient binder to wet the pigment particles and the resultant paint is powdery and easily scraped from the panel.

The small loss in reflectance of only 4.5% at 440 mμ for the methyl-phenyl gum stock, paint P-2, was surprising in light of our experience with phenyl-containing silicones in general. Comparable stabilities were not observed in the classical phenyl-methyl resins. It is suspected that the relative stability of P-2 resulted from the lower phenyl/methyl ratio compared with resins such as Dow Corning 806A. The gum stock was not studied further because of the superior stability of pure methyl silicones (see Section VIII).

Coatings P-9, P-10, P-12, P-14, P-15, and P-16 were also pigmented at a very high PBR and their respective critical pigment volume concentrations were probably exceeded, although fairly good adhesion was observed in these six paints. Of all the nonsilicone paints, P-14 showed the best resistance to yellowing. This paint was the acetone dispersion of Kel-F 8213 pigmented with SP 500 zinc oxide.

Reflectance curves for the 380- to 700-mμ wavelength region before and after irradiation are presented for paints P-4, P-10, P-14, and P-19 in Figures 30 through 33, respectively.

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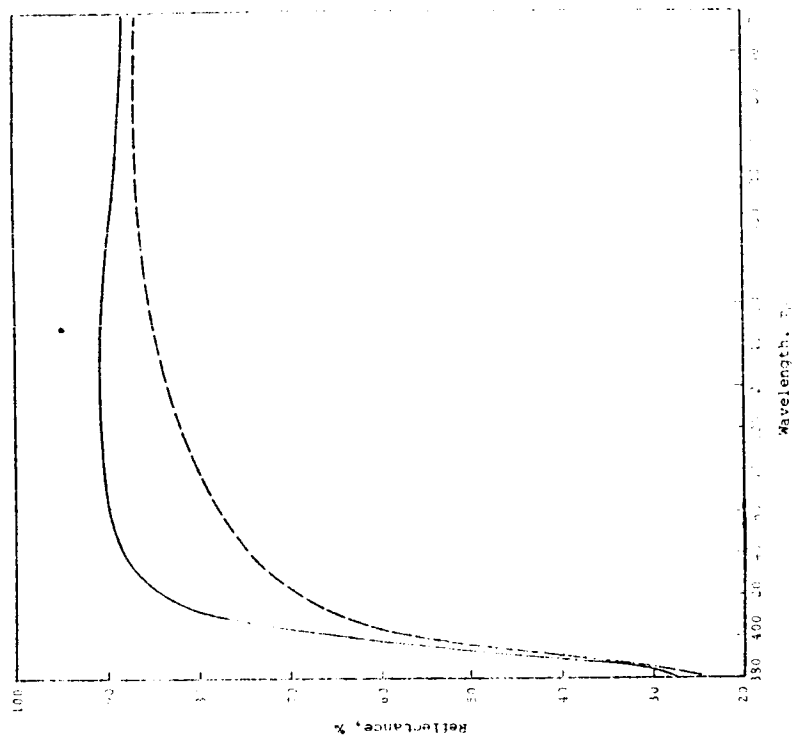


FIGURE 19

EFFECT OF 100 EHM IN VACUUM ON VISIBLE SPECTRAL REFLECTANCE OF COATING P-10

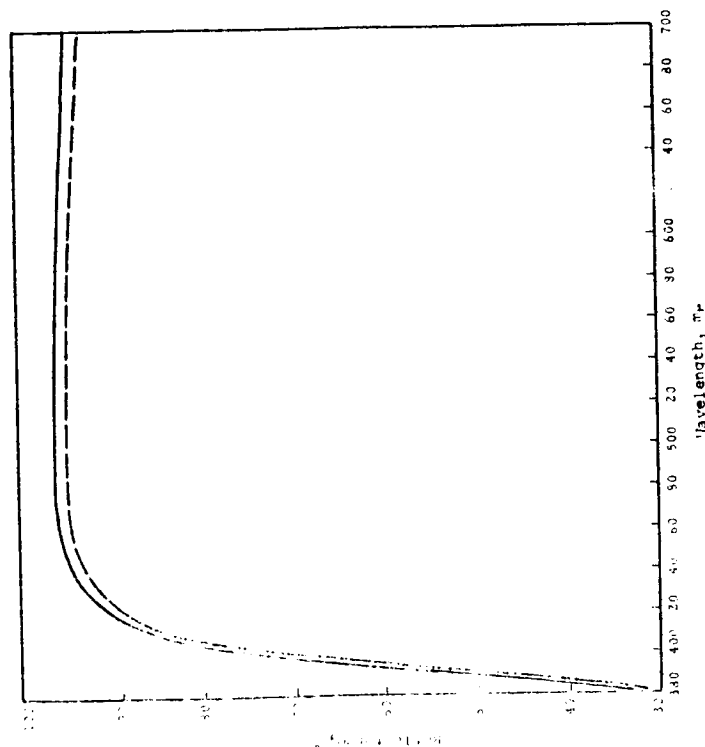


FIGURE 20

EFFECT OF 100 EHM IN VACUUM ON VISIBLE SPECTRAL REFLECTANCE OF COATING P-14

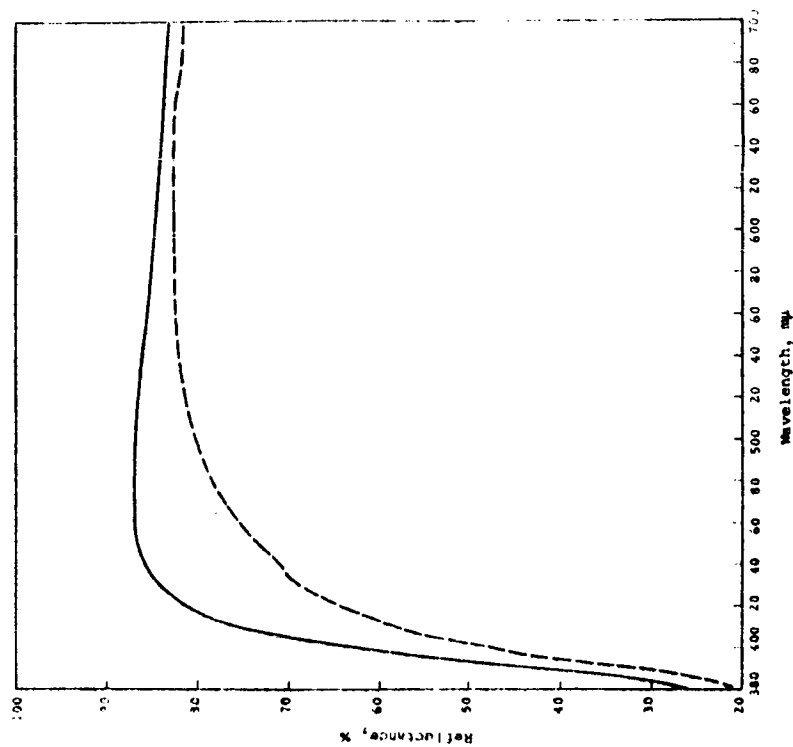


FIGURE 31
EFFECT OF 108 ESI IN VACUUM ON VISIBLE
SPECTRAL REFLECTANCE OF COATING F-19

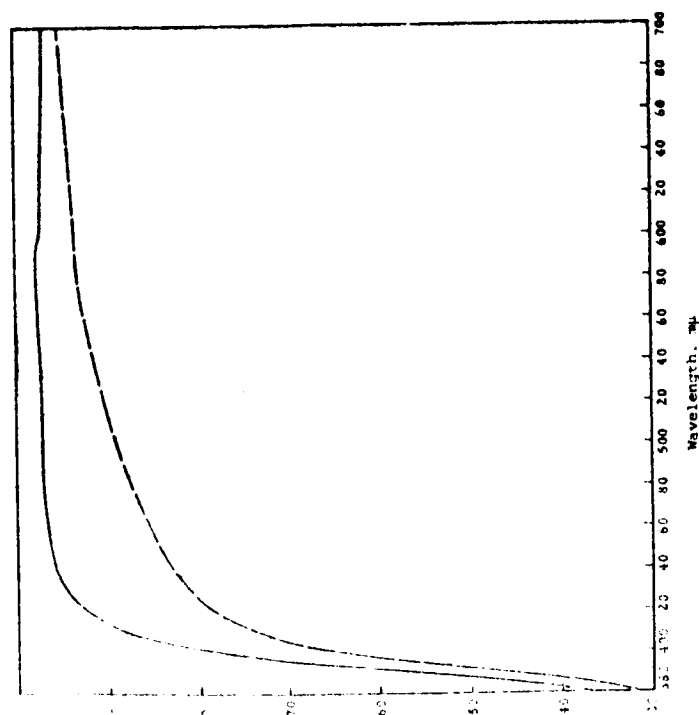


FIGURE 32
EFFECT OF 108 ESI IN VACUUM ON VISIBLE
SPECTRAL REFLECTANCE OF COATING P-14

VIII. ZINC OXIDE-PIGMENTED METHYL SILICONE PAINTS

A. Materials

As a result of the pigment and inorganic screening investigations, the pigmentation of silicone-based paints was confined essentially to the use of SP 500 zinc oxide. Rutile titanium dioxide and zinc sulfide were used in several instances for the purpose of comparison.

Except for two phenyl-methyl silicone paints, efforts were devoted primarily to methyl silicone or polydimethylsiloxane, polymers. The studies were divided into two phases: (1) evaluation of commercially available methyl silicone polymers and (2) synthesis and evaluation of experimental methyl silicone resins.

B. Paint Formulation

Except as noted, all the paints were ground in a porcelain jar mill for about 16 hours at approximately two-thirds critical speed. The critical speed (rpm) is given by⁸:

$$W_{Cs} = \frac{54.2}{\sqrt{R}}$$

where R is the radius of the mill (feet). The only ingredients used were pigment, vehicle, and solvent. Thus the possibilities of volatilization as well as photooxidation of additives at reduced pressure were eliminated.

The paints were made by charging an amount of the premixed paint to the mill sufficient to just fill the void space when the mill was one-half full of grinding stones. The premixed paint contained enough solvent to make a thin paste on grinding. The paint was reduced to a total solids content of 40% by volume at the completion of grinding. Except for paint S-17, catalysts were not a part of the mill charge but were added only as paint was required. The coatings were applied with a Paasche type AUTF airbrush at about 30 psi.

The formulation data for all the silicone paints are given in Table 17. Pigment/binder ratios are shown as both weight and volume ratios. Weight ratios are designated PBR (pigment/binder ratio). Volume ratios are designated PVC

⁸DallaValle, J. M., "Micromeritics," Pitman Publishing Corp. 1943.

Table 17
FORMULATION DATA FOR SILICONE PAINTS

| Paint No. | Ingredients, parts by wt. | PVC, % | PBR | Solids, % by vol. |
|-----------|---|-----------|------|----------------------|
| S-1 | Superlith XXXN zinc sulfide 107.5 806A resin 100.0 Toluene 37.0 | 40 | 2.15 | 40 |
| S-2 | SP 500 zinc oxide 156.0 R-621 resin 100.0 Xylene 40.0 | 40 | 3.10 | 40 |
| S-3 | SP 500 zinc oxide 141.0 XR-6-1057 resin 173.0 Tetrabutoxy titanium (TBT) 3.0 Toluene 108.0 | 20 | 1.19 | 40 |
| S-4 | SP 500 zinc oxide 45.0 R-1 exptl. resin soln. 111.0 | 25 | 1.35 | 26 |
| S-5 | SP 500 zinc oxide 93.4 XR-6-0049 resin 100.0 Xylene 38.0 | 25 | 1.80 | 40 |
| S-6 | SP 500 zinc oxide 186.8 LTV-602 polymer 100.0 SRC-04 catalyst 1.0 Toluene 171.0 | 25 | 1.87 | 40 |
| S-7 | SP 500 zinc oxide 140.1 LTV-602 polymer 100.0 SRC-05 catalyst 0.5 Toluene 160.0 | 20 | 1.40 | 40 |
| S-8 | SP 500 zinc oxide 112.0 R-2 exptl. resin soln. 100.0 Toluene 67.0 | 25 | 1.70 | 40 |
| S-9 | SP 500 zinc oxide 94.8 R-3 exptl. resin soln. 100.0 Toluene 43.6 | 25 | 1.70 | 40 |
| S-10 | SP 500 zinc oxide 77.5 R-4 exptl. resin soln. 100.0 Xylene 17.7 | 25 | 1.78 | 40 |
| S-11 | SP 500 zinc oxide 123.6 R-5 exptl. resin soln. 104.0 Toluene 86.0 | 25 | 1.63 | 40 |

| | | | | | |
|------|---|---------------------------------------|----|------|----|
| S-12 | SP 500 zinc oxide LTV-602 polymer SRC-05 catalyst Toluene | 186.8 100.0 0.5 170.0 | 25 | 1.87 | 40 |
| S-13 | SP 500 zinc oxide LTV-602 polymer SRC-05 catalyst Toluene | 240.0 100.0 0.5 183.8 | 30 | 2.40 | 40 |
| S-14 | Titanox RA-10 rutile 806A resin Toluene | 73.0 100.0 24.0 | 30 | 1.46 | 40 |
| S-15 | SP 500 zinc oxide R-5 exptl. resin Toluene | 212.0 100.0 157.0 | 30 | 2.12 | 40 |
| S-16 | SP 500 zinc oxide R-7 exptl. resin Toluene | 163.0 100.0 150.0 | 25 | 1.64 | 40 |
| S-17 | RA-NC rutile 808 resin Tetrabutoxy titanium (TBT) n-Butanol Toluene | 140.0 100.0 1.0 47.0 24.0 | 45 | 2.80 | 40 |
| S-18 | SP 500 zinc oxide SR-80 resin | 48.0 100.0 | 25 | 1.45 | 31 |
| S-19 | SP 500 zinc oxide R-5 exptl. resin Toluene | 268.0 100.0 176.0 | 35 | 2.68 | 40 |
| S-20 | SP 500 zinc oxide R-7 exptl. resin Toluene | 210.0 100.0 160.0 | 30 | 2.10 | 40 |
| S-21 | SP 500 zinc oxide E-P 414 zinc oxide R-5 exptl. resin Toluene | 134.0 134.0 100.0 176.0 | 35 | 2.68 | 40 |
| S-22 | SP 500 zinc oxide R-5A exptl. resin Silicure Z-775 Toluene | 213.0 100.0 0.5 126.0 | 35 | 2.13 | 40 |
| S-23 | SP 500 zinc oxide R-5B exptl. resin Tetrabutoxy titanium (TBT) Toluene | 255.0 100.0 1.0 168.0 | 35 | 2.55 | 40 |

Table 17 (cont.)

| Paint No. | Ingredients, parts by wt. | PVC, % | PBR | Solids, % by vol. |
|-----------|---|-----------|------|----------------------|
| S-24 | SP 500 zinc oxide 255.0 R-5B exptl. resin 100.0 Silicure Z-775 0.5 Toluene 168.0 | 35 | 2.55 | 40 |
| S-25 | SP 500 zinc oxide 213.0 R-5A exptl. resin 100.0 Tetrabutoxy titanium (TBT) 1.0 Toluene 126.0 | 35 | 2.13 | 40 |
| S-26 | SP 500 zinc oxide 373.0 LTV-602 polymer 100.0 SRC-05 catalyst 0.5 Toluene 214.0 | 40 | 3.73 | 40 |
| S-27 | SP 500 zinc oxide 304.0 LTV-602 polymer 100.0 SRC-05 catalyst 0.5 Toluene 197.0 | 35 | 3.04 | 40 |
| S-28 | Titanox RA-10 rutile 180.0 LTV-602 polymer 100.0 SRC-05 catalyst 0.5 Toluene 183.8 | 30 | 1.80 | 40 |
| S-29 | SP 500 zinc oxide 264.0 R-8 exptl. resin 100.0 Tetrabutoxy titanium (TBT) 1.0 Toluene 176.0 | 35 | 2.64 | 40 |
| S-30 | SP 500 zinc oxide 48.0 81932 resin 100.0 Tetrabutoxy titanium (TBT) 1.0 | 35 | 1.45 | 31 |
| S-31 | SP 500 zinc oxide 316.0 R-8 exptl. resin 100.0 Tetrabutoxy titanium (TBT) 1.0 Toluene 179.0 | 40 | 3.16 | 40 |
| S-32 | TiPure R-900-1 rutile 237.0 LTV-602 polymer 100.0 SRC-05 catalyst 0.5 Toluene 198.5 | 35 | 2.27 | 40 |

| | | | | | |
|----------|---------------------------------------|-------|----|------|----|
| S-33 | SP 500 zinc oxide | 316.0 | 40 | 3.16 | 40 |
| | R-9 exptl. resin | 100.0 | | | |
| | Tetrabutoxy titanium (TBT) | 1.0 | | | |
| | Toluene | 225.0 | | | |
| ZW-60 | Zinc sulfide | | 60 | | |
| | 808 resin | | | | |
| | Tetrabutoxy titanium | | | | |
| ZNO-40 | Zinc oxide | | 40 | | |
| | 808 resin | | | | |
| | Tetrabutoxy titanium | | | | |
| Q-9-0106 | Zinc oxide | | 25 | | |
| | Proprietary methyl silicone elastomer | | | | |
| Q-9-0107 | Rutile | | 25 | | |
| | Proprietary methyl silicone elastomer | | | | |
| Q-9-0108 | Zinc sulfide | | 15 | | |
| | Proprietary methyl silicone elastomer | | | | |

ZW-60
and ZNO-40
furnished
by JPL

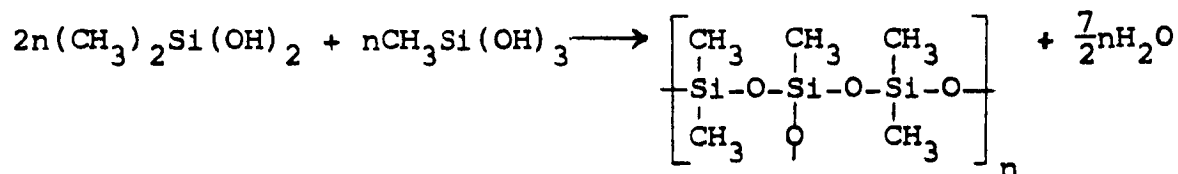
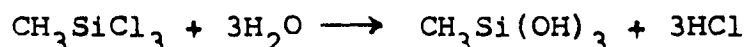
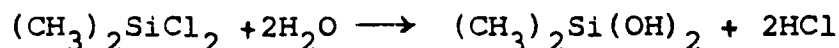
Q-9-0106,
Q-9-0107,
and Q-9-0108
furnished by
Dow Corning

Dow Corning: 806A resin, XR-6-1057 resin, XR-6-0049 resin, and 808 resin.
Du Pont: Tetrabutoxy titanium (TBT) and TiPure R-900-1 rutile.
Eagle-Picher: E-P 414 zinc oxide.
General Electric: LTV-602 polymer, SRC-04 catalyst, SRC-05 catalyst,
SR-80 resin, and 81932 resin.
National Lead: Titanox RA-10 rutile and Titanox RA-NC rutile.
New Jersey Zinc: SP 500 zinc oxide.
Nuodex Products: Silicure Z-775.
C. J. Osborn Co.: Superlith XXXN zinc oxide.
Union Carbide: R-621 resin.

(pigment volume concentration). The interaction of light with pigmented systems depends upon the volume and the surface area rather than upon concentrations by weight. In other words, two white pigments of different densities can be compared as paints only at equal volume concentrations.

C. Synthesis of Experimental Methyl Silicone Resins

The general reaction scheme for methyl silicone resins is given by Rochow and Gilliam⁹ as:



A mixture of mono- and disubstituted silicon halides (or ethoxy esters) is hydrolyzed, and the resultant silanetriols and silanediols are condensed to the resinous product. The composition of the resin is controlled by Me/Si, the molar ratio of methyl groups to silicon atoms. Me/Si is essentially the same for both the reactant mixture and the product. Methyl silicone polymers prepared in this way with Me/Si less than 1.2 are sticky syrups which cure at room temperature to hard brittle solids. Resins with Me/Si greater than 1.5, and especially greater than 1.7, are oily, slightly volatile liquids which cure to soft gels only after prolonged heating at 200°C.⁹

Relevant data on the various experimental silicones are tabulated in Table 18. Molecular weights were obtained on a Mechrolab vapor pressure osmometer, model 301A. The instrument is known as a "thermoelectric" type of osmometer.¹⁰

⁹Rochow, E. G. and Gilliam, W. F., The Journal of the American Chemical Society, Vol. 63, p. 798, 1941.

¹⁰Brody, A. P. et al, Journal of Physics and Colloid Chemistry, Vol. 55, p. 304, 1951.

Table 18

DATA ON EXPERIMENTAL METHYL SILICONE RESINS

| Experimental Silicone No. | Corresponding Paint No. | Silane Derivative (X) | Mol Ratio MeSiX ₃ /Me ₂ SiX ₂ | Mol Ratio Me/Si |
|------------------------------|----------------------------|-----------------------------|---|--------------------|
| R-1 | S-4 | Chloro | 2.4 | 1.29 |
| R-2 | S-8 | Chloro | 1.2 | 1.46 |
| R-3 | S-9 | Ethoxy | 1.2 | 1.46 |
| R-4 | S-10 | Ethoxy | 1.2 | 1.46 |
| R-5 | S-11 | Chloro | 1.6 | 1.38 |
| R-6 | None | Ethoxy | 2.4 | 1.29 |
| R-7 | S-16 | Chloro | 2.0 | 1.33 |
| R-5A | S-25 | Chloro | 1.6 | <1.38* |
| R-5B | S-23 | Chloro | 1.6 | |
| R-8 | S-31 | Chloro | 1.6 | <1.38* |
| R-9 | S-33 | Chloro | 1.6 | <1.38* |

* R-5A, R-8, and R-9 are products of molecular distillation and are higher molecular-weight analogs of R-5.

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The experimental resins were synthesized as follows.

Experimental Resin R-1:

Two-tenths moles (25.8 g) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 g) of methyltrichlorosilane (95%) were mixed in 300 g of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 30 min, to 1000 g of ice. The resultant water/ether phases were separated and the ether solution dried over anhydrous magnesium sulfate. The ether was evaporated, leaving the silicone resin in the form of an extremely hydrophobic, viscous liquid. The oil was taken up with sufficient xylene to make a 30% by wt. solution of the resin. The specific gravity of the resin solution was 0.996. Me/Si was calculated to be 1.29.

Experimental Resin R-2:

Four-tenths moles (51.6 g) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 g) of methyltrichlorosilane (95%) were mixed in 300 g of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 40 min, to 1000 g of ice. The ether layer was separated and washed with distilled water until a water layer neutral to litmus was obtained. The ether solution was dried over anhydrous magnesium sulfate and allowed to evaporate in a hood for 4 days. Me/Si was calculated to be 1.46. A 60% solution by vol. in toluene was prepared. The specific gravity of the resin solution was 1.015.

Experimental Resin R-3:

Four-tenths moles (59.2 g) of dimethyldiethoxysilane (90%) and 0.48 moles (35.5 g) of methyltriethoxysilane (90%) were mixed and added to 200 g of anhydrous ethyl alcohol. The mixture of silanes and alcohol was added to about 400 g of distilled water containing 10 g of 37% hydrochloric acid. The mixture was refluxed 3-1/2 hr. The resinous oil was separated by decantation, washed, and allowed to stand in a separatory funnel for 72 hr. The resin was again separated and diluted to 50% by vol. with toluene. The resin solution was then dried over Drierite. The specific gravity of the solution was 0.984. Me/Si was calculated to be 1.46.

Experimental Resin R-4:

Four-tenths moles (59.2 g) of dimethyldiethoxysilane (90%) and 0.48 moles (35.5 g) of methyltriethoxysilane (90%) were mixed with 150 g of 95% ethyl alcohol and added to 400 g of distilled water. To this mixture was added 22 ml of 37% hydrochloric acid, and the mixture was refluxed vigorously for 19 hr. A syrupy, viscous, colorless fluid of density greater than water resulted. The polymer was washed by decantation until a neutral test to litmus was obtained. Then 70 g of xylene was added, effecting separation of a water/organic phase. The organic layer was washed with distilled water twice and was dried over Drierite after weighing. The resultant solution contained 40% resin by vol. (47% by wt.), and the Me/Si of the polymer was calculated to be 1.46. The specific gravity of the resin solution was 0.965.

Experimental Resin R-5:

Three-tenths moles (38.7 g) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 g) of methyltrichlorosilane (95.0%) were mixed in 300 g of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 40 min, to 1000 g of ice. The ether layer was separated and washed once with distilled water. It was then washed with 5% solution of sodium bicarbonate, followed by three washings with distilled water. The ether solution was dried over Drierite and evaporated at reduced pressure, leaving a viscous, colorless resin. A resin solution in toluene was made at 67.4% solids by vol. The specific gravity of the resin solution was 1.040. Me/Si was calculated to be 1.33.

Experimental Resin R-6:

Four-tenths moles (59.2 g) of dimethyldiethoxysilane (90%) and 0.96 moles (171 g) of methyltriethoxysilane (90%) were mixed in 200 g of ethyl alcohol and added to 600 g of distilled water. To this mixture was added 33 ml of 37% hydrochloric acid, and the mixture was refluxed vigorously for 19 hr. A waxy colorless gum residue (solid) resulted in large yield. On drying the solid at reduced pressure, it was found to be insoluble in all common laboratory solvents. Me/Si was calculated to be 1.29.

Experimental Resin R-7:

Twenty-five one-hundredths moles (32.2 g) of dimethyldichlorosilane (99.4%) and 0.50 moles (74.8 g) of methyltrichlorosilane (95.0%) were mixed in 300 g of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 40 min, to 1000 g of ice. The ether layer was separated and washed with distilled water until a water layer neutral to litmus was obtained. The ether solution was dried over Drierite and evaporated at a reduced pressure, leaving a viscous, colorless resin. The specific gravity of the resin was 1.150. Me/Si was calculated to be 1.33.

Experimental Resins R-5A and R-5B:

The basic R-5 methyl silicone resin was prepared according to the procedure outlined above. The resultant stock resin (containing no solvent) was distilled at 150°C at 0.04 ± 0.01 mm Hg pressure in an ASCO '50' Rota-Film molecular still. The upper-molecular-weight fraction was collected as R-5A. Its molecular weight was found to be 2290. **NOTE:** The lower-molecular-weight fraction was redistilled at 150°C and 0.04 mm Hg pressure. Its upper fraction was then collected as R-5B. The molecular weight was found to be 958. The specific gravity of R-5A was 1.140 and that of R-5B was 1.181. The resins were decolorized with Atlas Powder's Darco Activated Carbon Q60.

Experimental Resin R-8:

The basic R-5 methyl silicone resin was prepared according to the procedure outlined above. The resultant stock resin (containing no solvent) was distilled at an average temperature of 108°C and 0.04 mm Hg pressure in an ASCO '50' Rota-Film molecular still. The upper-molecular-weight fraction was collected as R-8. Its molecular weight was found to be 2100, and its specific gravity was 1.182. The resin was decolorized with Atlas Powder's Darco Activated Carbon Q60.

Experimental Resin R-9:

The basic R-5 methyl silicone resin was prepared according to the procedure outlined above. The resultant stock resin (containing no solvent) was distilled at an average temperature of 100°C and 0.004 mm Hg pressure in an ASCO '50' Rota-Film molecular still. The upper-molecular-weight fraction was collected as R-9. Its molecular weight was found to be 2000, and its specific gravity was 1.190. The resin was decolorized with Atlas Powder's Darco Activated Carbon Q60.

D. Determination of Physical Properties

1. General

Commercial and experimental methyl silicone polymers were evaluated. The commercial polymers were Dow Corning's XR-6-0049, XR-6-1057, and XR-6-2000 and General Electric's LTV-602. XR-6-2000 and LTV-602 are methyl silicone potting compounds. A resin designated SR-80 was furnished by General Electric and was reported to be a zinc octoate cured methyl resin. A similar resin but without the catalyst was also furnished. It was designated No. 81932. The behavior of paints based upon SR-80 and No. 81932 when subjected to space simulation as well as infrared analysis, however, showed that these resins are not pure methyl polymers. The cohesive and adhesive strengths of zinc oxide paints based on XR-6-2000 were so poor that no further tests were made.

The first batch of XR-6-0049 formed an irreversible gel before it could be used, and paint S-5 (Table 17) was formulated from a second batch, with a shelf life of over 6 months.

XR-6-1057 was pigmented with SP 500 zinc oxide at PVCs of 20, 25, and 30%. All three coatings as well as a clear varnish of XR-6-1057 underwent catastrophic "checking" at the 360°F temperature required to cure the coatings. An air-drying modification of XR-6-1057 was prepared by careful addition of 1% tetrabutoxy titanium (TBT) in n-butanol. This resin solution was subsequently pigmented with SP 500 zinc oxide at 20% PVC and applied to aluminum substrates. The coating air-dried to the touch in 1 hour and formed a film capable of being evaluated in the space-simulation chamber. The coating was designated S-3.

Paint S-6 is a zinc oxide-pigmented methyl silicone elastomer made from LTV-602 and General Electric's SRC-04 catalyst. The paint required over 2 weeks at 360 °F to cure tack-free. Subsequent coatings based on LTV-602 utilized General Electric's SRC-05 catalyst and their proprietary primers SS-4004 and SS-4044. These coatings all cured within 48 hours at room temperature. Paints formulated at higher PVCs cured at room temperature in 18 hours or less. This behavior is possibly due to greater porosity in the more highly pigmented systems, permitting faster solvent evaporation. Adhesion of LTV-602 paints was poor when the primers were not used. In fact, unprimed coatings were easily stripped intact from surfaces as large or larger than 1 square foot. The adhesion of the primed material was adequate, as determined by subsequent tests. Another problem with the elastomeric coatings was their affinity for dirt, dust, and debris.

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Although it was virtually impossible to keep their surfaces clean, the collected dirt was easily removed by wiping with a soft damp cloth.

The curing properties of the paints containing the experimental silicones derived from silicon halides were essentially as expected. The coating containing the lowest Me/Si, 1.29 (Table 18), cured in only 1 hour at 330°F. some checking occurred on heating to a slightly higher temperature. The coating with the highest Me/Si, 1.46, required 16 hours at 300°F to cure. The coating with an intermediate Me/Si, 1.38, cured in about 16 hours at 260°F.

The molecularly distilled resins based upon the R-5 stock did not cure in 16 hours at 300°F. When catalyzed with zinc octoate (Silicure Z-775), they usually cured in only 15 minutes at 300°F to a very hard, brittle, glossy film which could not be marred with a fingernail. However, coatings cured with zinc octoate failed on thermal shock cycling and formed long cracks on cooling after being heated to temperatures in excess of 300°F. When these same formulations were cross-linked with tetrabutoxy titanium (TBT), they cured in 1 hour at 300°F to a tough, equally hard, glossy film which withstood exposure to 500°F and ten or more thermal shock cycles. Exposure to 500°F for 1 hour or more improved their hardness but changed the surfaces from glossy to semiglossy.

The methyl silicones derived from silicon esters required higher baking temperatures to cure compared with those derived from silicon chlorides at the same Me/Si. Paints based on the resins derived from silicon esters appeared to "haze" at the curing temperatures. In addition, they were highly porous and soft but brittle coatings which offered no physical advantages over the coatings based on chlorosilane derived resins.

With the exception of S-3, which was catalyzed with tetrabutoxy titanium, all the silicone paints studied had adequate shelf lives. The main problem encountered was pigment settling, which occurred rapidly in the methyl resin coatings. No difficulties were experienced in redispersing the pigment in these coatings, however. The film properties and curing conditions of all the silicone paints are presented in Table 19.

Paints S-1, S-2, S-14, and S-17 were formulated for purposes of comparison with the methyl silicones (See Table 17). They all are phenyl-methyl silicones and therefore require curing at 400°F or higher. S-14 was formulated as a substrate for zinc oxide-pigmented methyl silicones and is discussed in a later section. S-17 was formulated for the Round Robin Testing Program and was designated as TC-50.19 for that program.

Table 19
CURING CONDITIONS AND FILM PROPERTIES
OF THE SILICONE PAINTS

| Paint No. | Cure | Film Properties |
|-----------|--|--|
| S-1 | 4 hr at room temp. + 1 hr at 400°F | Film integrity, appearance, and adhesion excellent. Good gloss. |
| S-2 | 4 hr at room temp. + 1 hr at 400°F | Film integrity, appearance, and adhesion excellent. Good gloss. |
| S-3 | 16 hr at room temp. | Film hard and brittle. Appearance and gloss good. Cracked off on heating to 300°F. |
| S-4 | 4 hr at room temp. + 1 hr at 330°F | Film integrity and adhesion good. Checked on heating to 360°F for 1 hr. Semiglossy. |
| S-5 | 4 hr at room temp. + 1 hr at 330°F | Film integrity and adhesion good. Checked severely on heating to 360°F. |
| S-6 | 12 hr at room temp. + 2 wk at 360°F | Adhesion poor. Not thoroughly cured. Good gloss. |
| S-7 | 16 hr at room temp. | Very slight tackiness. Cured on heating to 150°F; cured after 48 hr at room temp. Resilient, excellent gloss. Required primer. |
| S-8 | 4 hr at room temp. + 16 hr at 300°F | Film integrity and adhesion good. Flat. Required temp. above 300°F to cure in less than 16 hr. |
| S-9 | 4 hr at room temp. + 18 hr at 300°F | Did not cure until baked 2 hr at 400°F (in addition to 18 hr at 300°F). Checked severely. |
| S-10 | 4 hr at room temp. + 2 hr at 450°F | Film integrity and adhesion good. Flat. |
| S-11 | 4 hr at room temp. + 24 hr at 260°F | Film integrity and adhesion good to excellent. Flat. Vitreous-like. |
| S-12 | 18 hr at room temp. | Resilient, high-gloss film with good adhesion when primed. |
| S-13 | 13 hr at room temp. | Resilient, high-gloss film with good adhesion when primed. |
| S-14 | 4 hr at room temp. + 16 hr at 300°F | Film integrity, appearance, and adhesion excellent. Excellent gloss. |
| S-15 | 4 hr at room temp. + 3 hr at 300°F | Hard, porous surface with good adhesion. |
| S-15 | 4 hr at room temp. + 40 hr at 300°F | Hard, brittle, porous coating showing some microcracks on cooling. Good adhesion. |

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| | | |
|------|---|--|
| S-15 | 4 hr at room temp. +15 hr at 400 F | Failed ("popped off") on cooling. |
| S-16 | 4 hr at room temp. +40 hr at 300 F | Hard, nonglossy surface showing good adhesion and appearance. |
| S-17 | 4 hr at room temp. + 1 hr at 300 F | Film integrity, appearance, and adhesion good. |
| S-18 | 4 hr at room temp. + 2 hr at 300 F | Film integrity, appearance, and adhesion very good. Tough and hard. |
| S-19 | 4 hr at room temp. + 3 hr at 300 F | Film integrity, appearance, and adhesion good. Semiglossy. Hard. Porous. |
| S-20 | 4 hr at room temp. + 2 hr at 300 F | Hard, porous surface showing good adhesion and appearance. Showed small edge cracks after several hr at 300 F. |
| S-21 | 4 hr at room temp. + 3 hr at 300 F | Film integrity, appearance, and adhesion good. Hard. Porous. |
| S-22 | 4 hr at room temp. + 1 hr at 300 F | Hard, brittle film with good adhesion. Semiglossy. |
| S-23 | 4 hr at room temp. + 1/2 hr at 300 F | Hard, brittle coating with good adhesion. Semiglossy. Somewhat porous. |
| S-24 | 4 hr at room temp. + 1/4 hr at 300 F | Hard, brittle coating with good adhesion. Semiglossy. Somewhat porous. |
| S-25 | 16 hr at room temp. + 1 hr at 500 F | Hard, could not be scratched with finger-nail. Withstood 1 hr at 500 F. Glossy. |
| S-26 | 16 hr at room temp. | Crumbly surface. Poor adhesion even when primed. Difficult to spray-apply. |
| S-27 | hr at room temp. | Difficult to spray-apply. Soft, semiglossy surface. Good adhesion when primed. Resilient. |
| S-28 | 16 hr at room temp. | Soft, somewhat tacky. Glossy, with fair adhesion. |
| S-29 | 24 hr at room temp. +18 hr at 250 F | Hard, glossy coating which resisted scratching. Good adhesion. Withstood 1 hr at 500 F. |
| S-30 | 16 hr at room temp. +18 hr at 250 F | Hard, brittle, glossy film with good adhesion. |
| S-31 | 16 hr at room temp. + 1 hr at 300 F + 2 hr at 250 F | Hard, brittle, glossy film with good adhesion. Withstood 1 hr at 500 F. |
| S-32 | 16 hr at room temp. | Soft, resilient film with excellent gloss and good adhesion when primed. |
| S-33 | 4 hr at room temp. + 1 hr at 300 F | Hard, brittle, glossy film with good adhesion. Withstood 1 hr at 500 F. |

2. Thermal Shock

The thermal-shock test was the same as that used for the inorganic coatings. All coatings listed in Tables 17 and 19 except S-5, S-6, S-9, S-14, S-17, S-28, S-30, and S-32 were tested. The phenyl-methyl paints S-1 and S-2 and the paint S-18, based on General Electric's SR-80, flaked and cracked on the first cycle. S-20 showed small cracks along the specimen's edge after 10 thermal-shock cycles. The remainder of the coatings, all 100% methyl silicone paints, withstood 10 cycles of 200 to -320 to 200°F.

3. Torsion

The results of torsion tests on six silicone paints are presented in Table 20. Paint S-1, the zinc sulfide-806A phenyl silicone paint, failed the 90° torsion tests, while S-2, the zinc oxide-R-621 phenyl silicone paint, was stressed 90° without failure. Of significance is the fact that S-4 exhibited poorer twist resistance than S-8. S-4 contains a polymer with an Me/Si of 1.29, whereas S-8 contains a polymer with an Me/Si of 1.46. The PVC of both paints was 25%, and the resins were both synthesized from appropriate mixtures of chlorosilanes. The Me/Si of the polymers used in paints S-19, S-29, S-31, and S-33 was 1.38.

The torsional stress resistance of several other organic coatings is presented in Table 21 for purposes of comparison.

4. Abrasion

Three methyl silicone paints were applied to 4- x 4-inch panels for abrasion resistance tests with the Taber Abraser. Each sample received 100 revolutions at forces of either 125 or 500 G. As expected, the abrasion resistance of the methyl silicones (Table 22) was not as good as that of the inorganic paints. Although the loss in weight of paint S-7 was of the same order of magnitude as that of the inorganic paints, the loss was due less to hardness than to resiliency.

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Table 20
TORSIONAL STRESS RESISTANCE OF SILICONE PAINTS

| <u>Paint No.</u> | <u>Cure</u> | <u>Thickness, mils</u> | <u>Results of 90° Stress</u> |
|------------------|--|----------------------------|--|
| S-1 | Air-dried for 24 hr | 4 | Subsurface cracked at 82°. |
| | + 16 hr at 300°F | 5 | Cracked at 18°. |
| | + 2 hr at 400°F | 3 | Cracked at 75°. |
| S-2 | Air-dried for 24 hr | 4 | No failure. |
| | + 16 hr at 300°F | 4 | No failure. |
| | + 2 hr at 400°F | 4 | No failure. |
| S-4 | Air-dried for 24 hr | 3 | Cracked at grip at 52°. |
| | + 16 hr at 300°F | 3 | Cracked at grip at 47°, cracked at 85°. |
| | | 3 | Cracked at grip at 65°. |
| S-7 | Air-dried for 72 hr | 4.5 | No failure. |
| | | 4.5 | No failure. |
| | | 4.5 | No failure. |
| S-8 | Air-dried for 4 hr + 16 hr at 300°F | 4 | No failure. |
| | | 4 | No failure. |
| | | 4 | No failure. |
| S-10 | Air-dried for 4 hr + 2 hr at 450°F | 3+ | No failure. |
| | | 3+ | No failure. |
| | | 3+ | No failure. |
| | | 3+ | No failure. |
| S-19 | Air-dried for 4 hr + 2 hr at 300°F | 3+ | No failure. |
| | | | |
| S-29 | Air-dried for 4 hr + 3 hr at 300°F | 3+ | No failure. |
| | | 3+ | No failure. |
| S-31 | Air-dried for 4 hr + 3 hr at 300°F | 3+ | No failure. |
| | | | |
| S-33 | Air-dried for 4 hr + 1 hr at 300°F | 3 | No failure. |
| | | | |
| S-33 | Air-dried for 4 hr | 3 | No failure. |
| | + 1 hr at 300°F | | |
| | + 1 hr at 500°F | | |

Table 21

TORSIONAL STRESS RESISTANCE OF MISCELLANEOUS ORGANIC COATINGS

| Composition | Thickness, mils | Results of 90° Stress |
|--|--------------------|---|
| B-V A29550 acrylic-phenolic | 2 | No failure after 120°. |
| Leonite 201s | 4 | Subsurface cracked at 42°. No separation from aluminum substrate after 90°. |
| Leonite 201s and SP 500 ZnO | 5 | Subsurface cracked at 75°. No separation from aluminum substrate after 90°. |
| Butylated urea- formaldehyde and Epon 1007 | 7 | Subsurface cracked at 70°. No separation from aluminum substrate after 90°. |
| Marietta 6301 epoxy enamel | 3 | Subsurface cracked at 62°. No separation from aluminum substrate after 90°. |
| Silicone 806A and SP 500 ZnO | 4 | Subsurface cracked at 24°. Surface cracked at 42°. Separation from aluminum substrate at 52°. |

Table 22

ABRASION RESISTANCE OF SILICONE PAINTS

| Paint No. | Weight Loss, g | |
|-----------|------------------|------------------|
| | At 125 G | At 500 G |
| S-7 | 0.0098 | 0.0915 0.0532 |
| S-8 | 0.0929 | 0.2224 |
| S-10 | 0.0790 0.0661 | |

5. Film Strength of LTV-602 Paints

The film strength of the LTV-602 paints was determined on free, detached films of three paints, S-7, S-12, and S-13, pigmented at 20, 25, and 30% PVC. They were prepared by pouring portions of the catalyzed paint on a clean flat surface. The paint was allowed to cure for 48 hours, was stripped, and then was aged for 16 hours at 150°F. Tensile test specimens were prepared and were stressed on an Instron tensile testing machine. The data are presented in Table 23. Each value represents an average of four tests. The tensile strength increased and the elongation decreased with increasing PBR. Little difference in tensile strength due to increasing the PVC from 25 to 30% was observed, although this increase in PVC caused a significant decrease in elongation. An LTV-602 paint with a 40% PVC exhibited such poor cohesive strength that it was not tested.

Table 23

TENSILE STRENGTH AND ELONGATION OF LTV-602 PAINTS

| <u>Coating</u> | <u>PVC, %</u> | <u>Average Tensile Strength, psi</u> | <u>Average Elongation, ΔL, in.</u> |
|----------------|-------------------|--|---|
| S-7 | 20 | 313 | 3.42 |
| S-12 | 25 | 412 | 3.56 |
| S-13 | 30 | 415 | 2.80 |

E. Determination of Optical Properties

The effects of film thickness and PVC on the optical properties of several elastomeric paints are presented in Figures 34 and 35. The total normal emittance values (at 200°F) of S-7 and S-12 are presented in close proximity to the points on the graphs. The data confirm that thick coatings of approximately 10 mils are required to optimize reflectance and to avoid the necessity for thickness control. The effect of PVC on solar absorptance was pronounced only at lower film thickness, except for paint S-26, which was pigmented at 40% PVC. Little difference in solar absorptance was observed when paints S-7, S-12, S-13, and S-27 were applied at a film thickness of about 10 mils. On the other hand, considerably thinner coatings appeared to optimize emittance.

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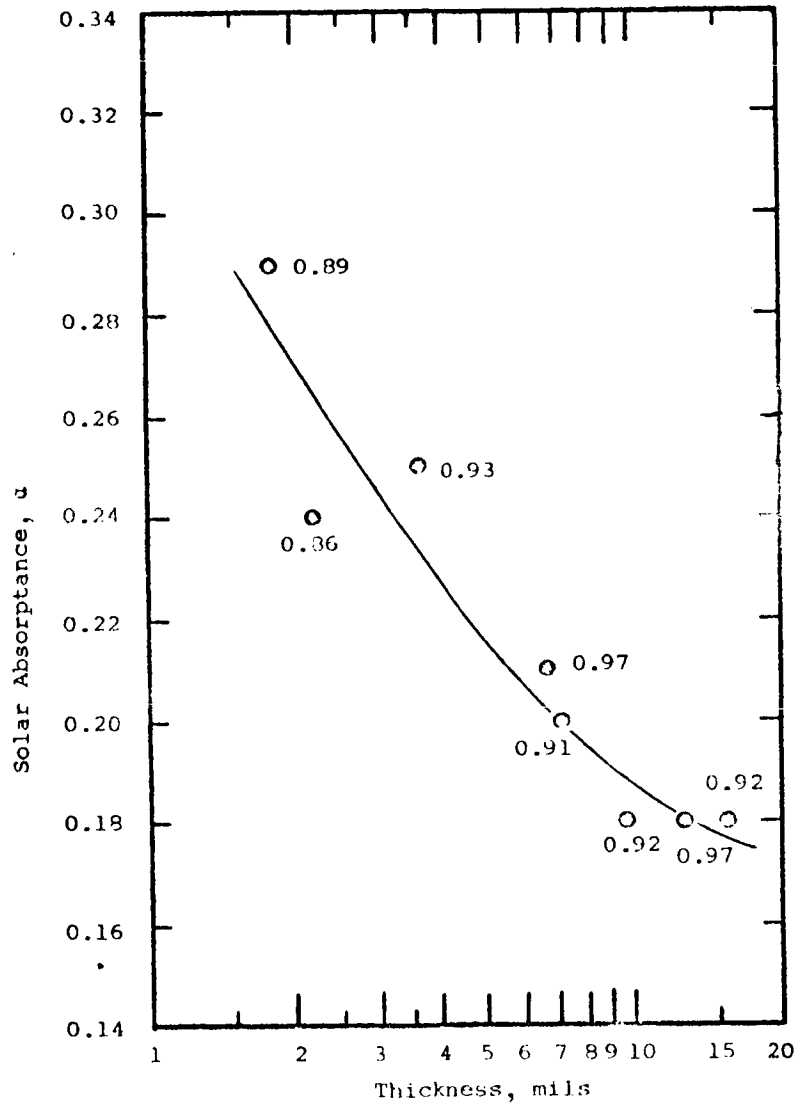


Figure 34

SOLAR ABSORPTANCE VERSUS THICKNESS IN PAINT S-7

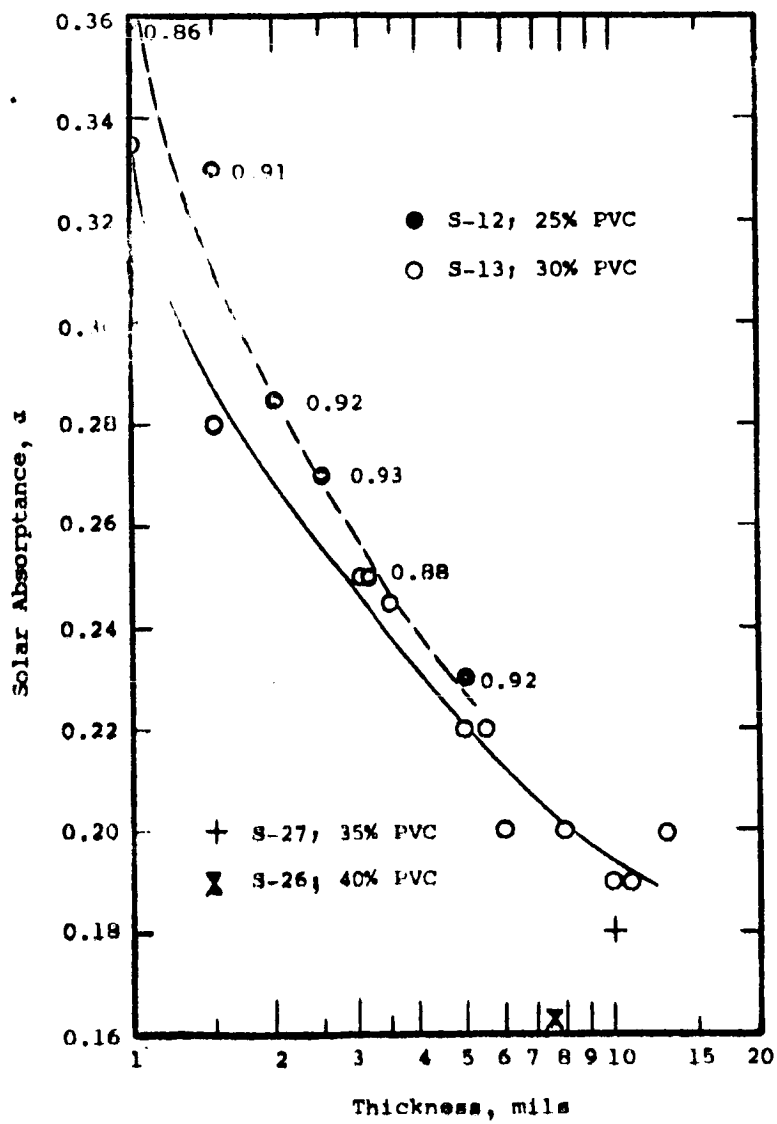


Figure 35

SOLAR ABSORPTANCE VERSUS THICKNESS
IN PAINTS S-12, S-13, S-26, AND S-27

In the infrared emitting region the paint is essentially an absorber; whereas in the region of the solar spectrum the paint is a mixture of two nonabsorbing, transparent materials, the silicone vehicle and the zinc oxide. Except for the ultraviolet region, where zinc oxide is a strong absorber, opacity and solar reflectance are achieved by scattering mechanisms. The strong dependency of solar absorptance on thickness, even for relatively thick films, is emphasized by the facts that (1) zinc oxide possesses a low refractive index compared with such pigments as rutile titanium dioxide and zinc sulfide and (2) its concentration in the paints is low.

Paint S-26 was pigmented at 40% PVC and possessed an exceptionally low solar absorptance of 0.16 at a thickness of only 7.5 mils. The low absorptance may be attributable to the fact that 40% represents a concentration equal to or greater than the critical PVC. Thus the coating possessed many pigment particles with an air interface and consequently had a higher average refractive index ratio, which resulted in greater scattering due to enhanced porosity throughout the coating. As a consequence of the excessive pigment concentration, the film was powdery and fragile and lacked cohesive strength sufficient to ensure its utility.

The effect of the film thickness of S-33 on its solar absorptance, total normal emittance, and the ratio of the two is presented in Figure 36. This paint was based on the molecularly distilled experimental resin R-9 with an $n_{\text{Me/Si}}$ of 1.38. It was pigmented with SP 500 zinc oxide at 40% PVC.

Coatings S-21 and S-19 were the same except that in S-21 Eagle-Picher's 414 zinc oxide was substituted for half the amount of SP 500 zinc oxide required for 35% PVC. The mean particle size of 414 pigment is 1.0μ , whereas that of SP 500 is 0.30μ . The influence of the larger particle size was manifested in the α_1 and α_2 of the unirradiated S-21 film (see Figure 37). The larger size more effectively scattered the long-wavelength light, resulting in α_1 and α_2 of 0.135 and 0.093, respectively, compared with 0.120 and 0.099 in S-19. The larger α_1 of both coatings compared with α_2 is due principally to the characteristic absorption of zinc oxide for ultraviolet light at wavelengths below 4000 Å.

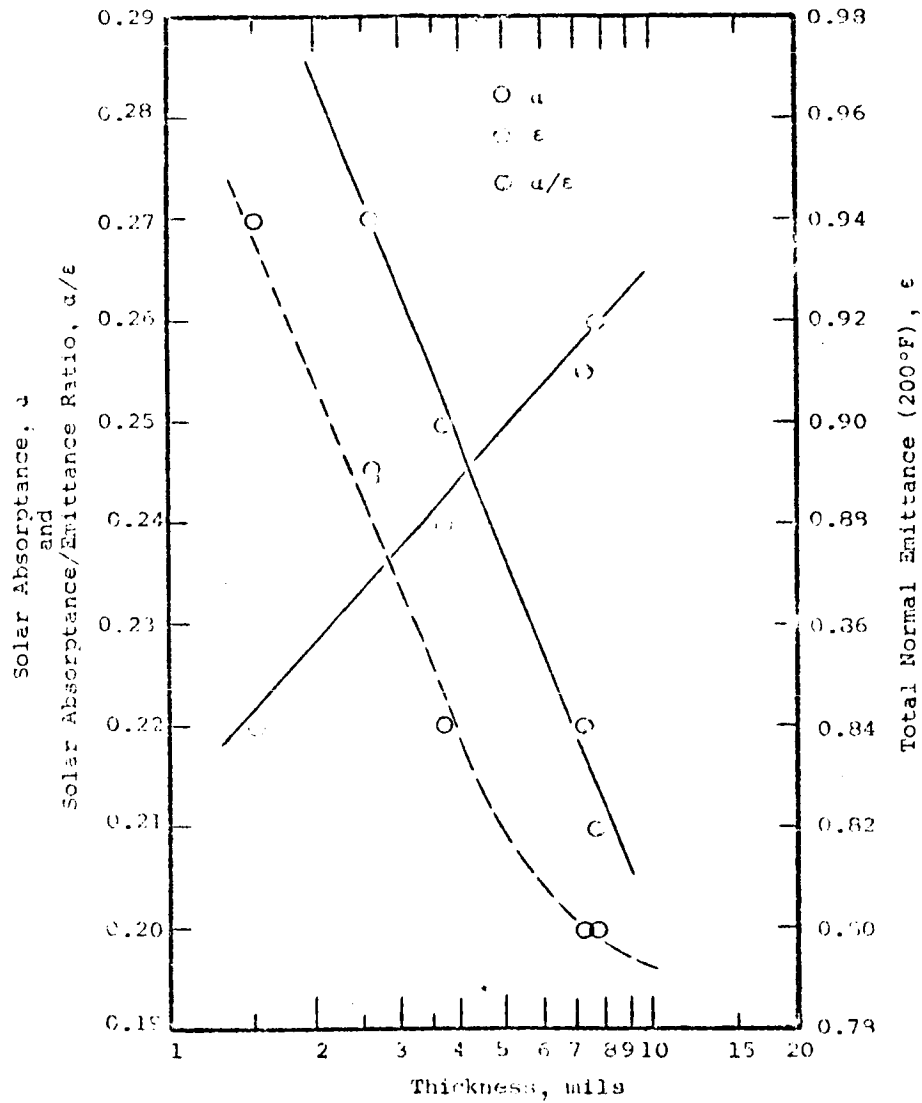


Figure 36

SOLAR ABSORPTANCE, SOLAR ABSORPTANCE/EMITTANCE RATIO,
AND TOTAL NORMAL EMITTANCE VERSUS THICKNESS IN PAINT S-33

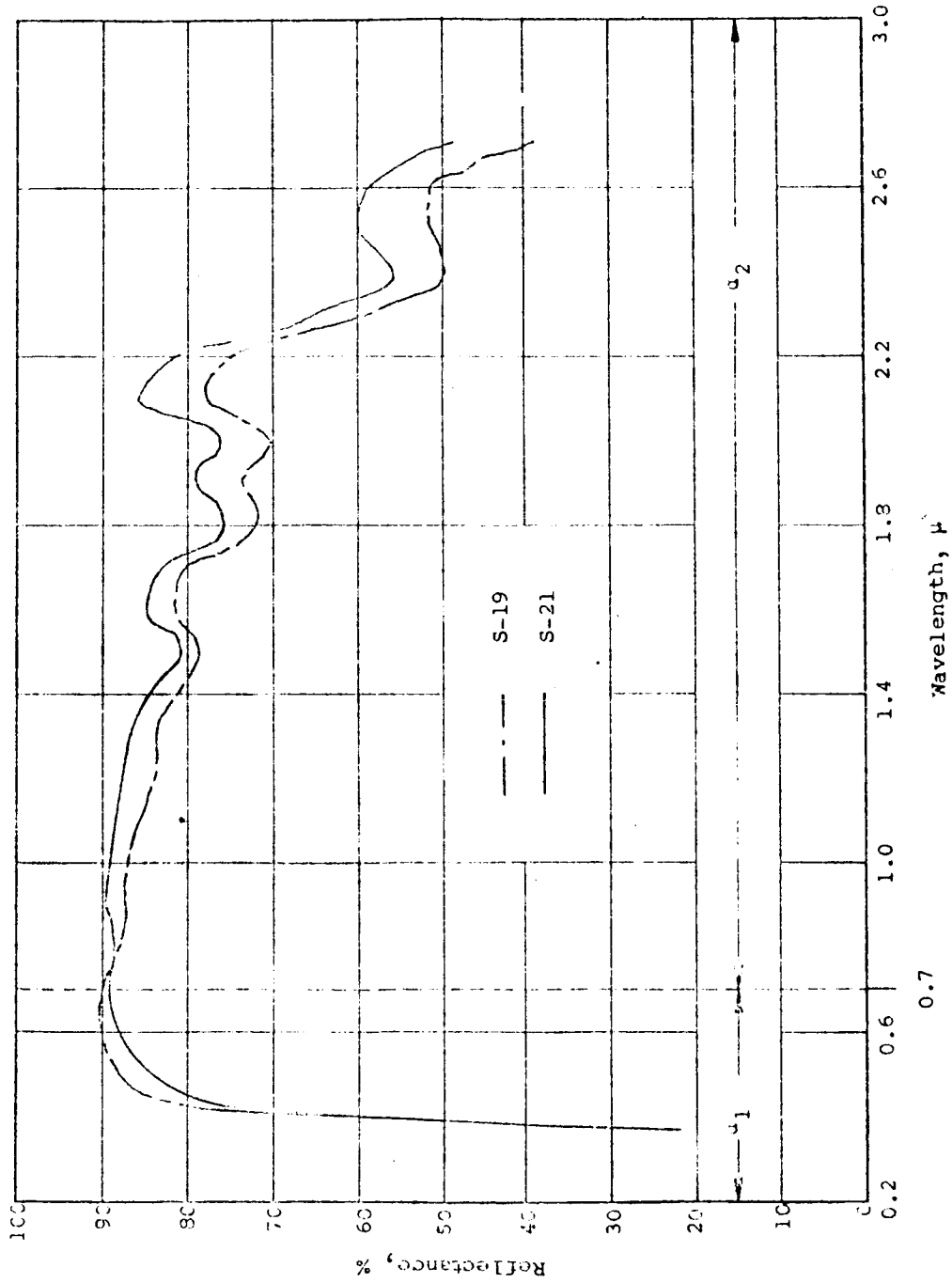


Figure 37
EFFECT OF PIGMENT PARTICLE SIZE ON SOLAR SPECTRAL REFLECTANCE OF PAINTS S-19 AND S-21

F. Stability to a Simulated Space Environment

1. Preliminary Studies

The results of the initial space-simulation tests on several silicone coatings are given in Table 24. Coatings S-1 through S-5 were irradiated in the oil-diffusion-pumped system (Test E); S-7, S-8, and S-10 were irradiated in the ion-pumped system (Test I). The two methyl-phenyl silicone paints, S-1 and S-2, exhibited severe degradation, as evidenced by the loss in reflectance at 440-m μ wavelength. Both S-7 and S-8 showed some loss in reflectance at 440-m μ wavelength. These losses appear almost as large as those observed in S-2, but the ultraviolet intensity was greater and the total exposure was increased 50%. Four methyl silicone paints, S-3, S-4, S-5, and S-10 exhibited reflectance changes of 1% or less, with several of the changes representing increases. The increases are considered to be a result of experimental errors such as viewing different measuring positions on the sample before and after exposure.

Although coatings S-3 and S-5 possessed exceptional stability to ultraviolet irradiation in vacuum, their poor physical properties in comparison with those of S-7, S-8, and S-10 precluded their further consideration. They were more difficult to apply, they were brittle, and they checked at moderate temperatures. Subsequent work was therefore confined to the LTV-602 and experimental methyl silicone resins.

2. Effect of Me/Si

The effect of varying the Me/Si of methyl silicone resins from 1.29 to 1.46 is presented in Table 25. Examination of the reflectance and solar absorptance changes at various exposures shows that the paints based on resins with lower Me/Si were superior.

The small change in solar absorptance of S-4, however, is belied by the severe decrease in reflectance at 440-m μ wavelength. This decrease in the visible was counterbalanced by an anomalous increase in reflectance in the near-infrared solar region as shown in Figure 38. While the anomaly cannot be explained at this time, it is interesting to compare coating S-4 with the inorganic paint Z-1 (see Figure 29). Resin R-1, the vehicle in S-4, has the lowest Me/Si, and possesses a structure which is more like that of the alkali silicates than any of the other experimental resins. Furthermore, S-4, like Z03, showed an increase in near-infrared reflectance on exposure to ultraviolet radiation in vacuum. R-1 was eliminated from further consideration, however, because of its inherent brittleness and failure when torsionally stressed to 90°.

Table 24

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF SEVERAL SILICONE PAINTS

| Paint No. | Composition | | F.D., % | Exposure | | Reflectance, % | |
|-----------|-------------|-----------------|---------|----------|--------------|----------------|--------------|
| | Pigment | Binder | | ESH | Solar Factor | 440 mμ | 600 mμ |
| S-1 | ZnS | 806A | 40 | 0 300 | . 3 | 84.4 63.0 | 89.0 87.3 |
| S-2 | SP 500 ZnO | R-621 | 40 | 0 300 | 3 | 85.2 77.8 | 83.3 81.5 |
| S-3 | SP 500 ZnO | XR-6-1057 (TBT) | 25 | 0 300 | 3 | 82.0 83.0 | 90.0 91.0 |
| S-4 | SP 500 ZnO | R-1 | 25 | 0 300 | 3 | 79.0 79.5 | 81.5 80.5 |
| S-5 | SP 500 ZnO | XR-6-0049 | 25 | 0 300 | 3 | 80.5 81.0 | 83.5 84.5 |
| S-7 | SP 500 ZnO | LTV-602 | 20 | 0 450 | 10 | 87.5 82.5 | 92.5 90.5 |
| S-8 | SP 500 ZnO | R-2 | 25 | 0 450 | 10 | 80.5 76.0 | 92.0 91.5 |
| S-10 | SP 500 ZnO | R-4 | 25 | 0 450 | 10 | 77.0 77.0 | 87.5 87.0 |

Table 25

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES
OF SILICONE PAINTS AS A FUNCTION OF He/Si
(PVC = 25%)

| Paint No. | Composition | | Exposure | | Reflectance | | Solar Absorp- tance, α |
|--------------|-------------|----------------|----------|-----------------|-------------|-------------|--|
| | Binder | He/Si | ESH | Solar Factor | 440 m μ | 600 m μ | |
| S-4 | R-1 | 1.29 | 0 | | 79.0 | 91.5 | |
| | | | 300 | 3 | 79.5 | 90.5 | |
| | | | 0 | | 83.0 | 85.5 | .26 |
| | | | 1460 | 9 | 71.0 | 81.5 | .27 |
| S-10 | R-7 | 1.33 | 0 | | 80.5 | 88.5 | .26 |
| | | | 615 | 9 | 78.0 | 87.0 | .27 |
| | | | 0 | | 81.5 | 88.5 | .27 |
| | | | 1600 | 11 | 78.5 | 86.0 | .27 |
| S-11 | R-5 | 1.38 | 0 | | 86.5 | 91.0 | .23 |
| | | | 1460 | 9 | 82.5 | 88.5 | .25 |
| S-8 | R-2 | 1.46 | 0 | | 80.5 | 92.0 | |
| | | | 450 | 10 | 76.0 | 91.5 | |
| | | | 0 | | 85.5 | 94.0 | .20 |
| | | | 1460 | 9 | 82.0 | 91.0 | .23 |

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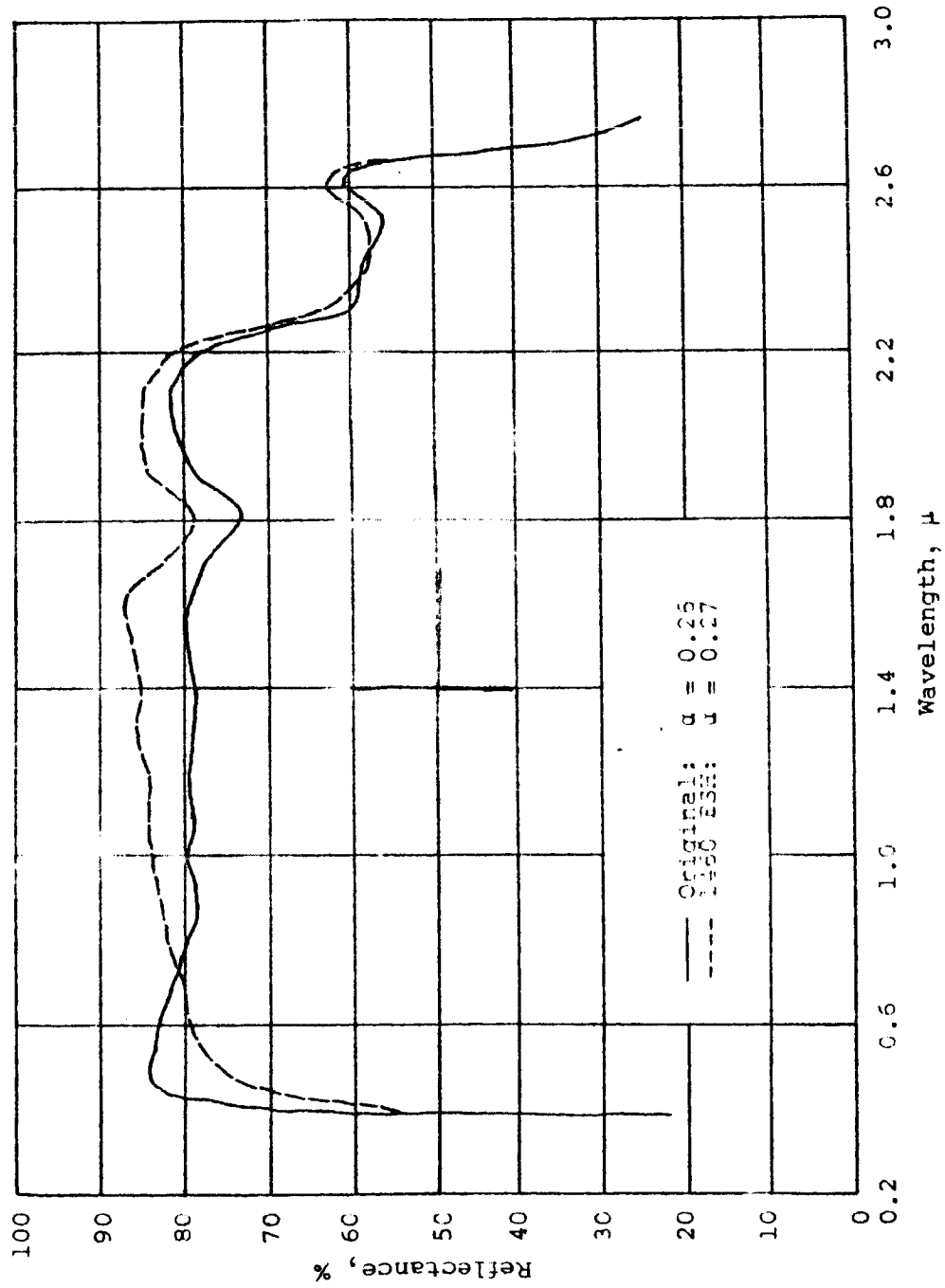


Figure 38
EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-4

Like paint S-4, coating S-16 degraded in the visible region but showed no solar absorptance change because it increased in near-infrared reflectance. The spectral reflectance curves of S-16 are presented in Figure 39.

The effects of exposure to 1460 ESH on the reflectance of coatings S-11 and S-8 are presented in Table 25 and Figures 40 and 41. S-11 was based on a resin with an Me/Si of 1.38, while S-8 was based on resin R-2, with an Me/Si of 1.46. There was little difference in the reflectance losses exhibited by the two paints as shown in Table 25. However, examination of the reflectance curves presented in Figures 40 and 41 explains the 0.03 increase in the solar absorptance of S-8 compared with 0.02 for S-11.

Thus, it can be seen that the selection of resin R-5 rather than R-7 for further evaluation and for use as a stock polymer for molecular distillation studies was somewhat arbitrary. The decision was based on the supposition that an increase in cross-linking and molecular weight probably accompanies molecular distillation. Such an increase coupled with the fact that the R-7 stock resin was polymerized from a higher ratio of methyl trichlorosilane to dimethyl chlorosilane (see Table 19) would produce still more brittle, glassy resins. It will be remembered that small cracks appeared in coating S-20 (based on R-7) when thermally shocked.

In summary, coatings formulated from resins with an intermediate Me/Si of 1.33 or 1.38 showed the best overall properties. Paints formulated from resins with a lower Me/Si exhibited superior resistance to a simulated space environment but were brittle and were subject to torsional failure. On the other hand, coatings based on resins with a higher Me/Si had poorer resistance to ultraviolet radiation in vacuum and required higher curing temperatures. An anomalous increase in reflectance on irradiation was noted for a paint based on a resin with an Me/Si of 1.29. The anomaly occurred in the near-infrared region of the spectrum and counterbalanced a reflectance decrease in the visible region, with the net result that little change in solar absorptance occurred. This phenomenon cannot be explained and was noted in several zinc oxide-pigmented potassium silicate paints also.

3. Paints Based on Resins of Intermediate Me/Si

The effects of ultraviolet irradiation in vacuum on zinc oxide paints containing resins R-7 and R-5 with Me/Si of 1.33 and 1.38 are presented in Table 26. The remarkable stability exhibited by these paints can be seen by the small changes in absorptance after exposure to over 1800 ESH.

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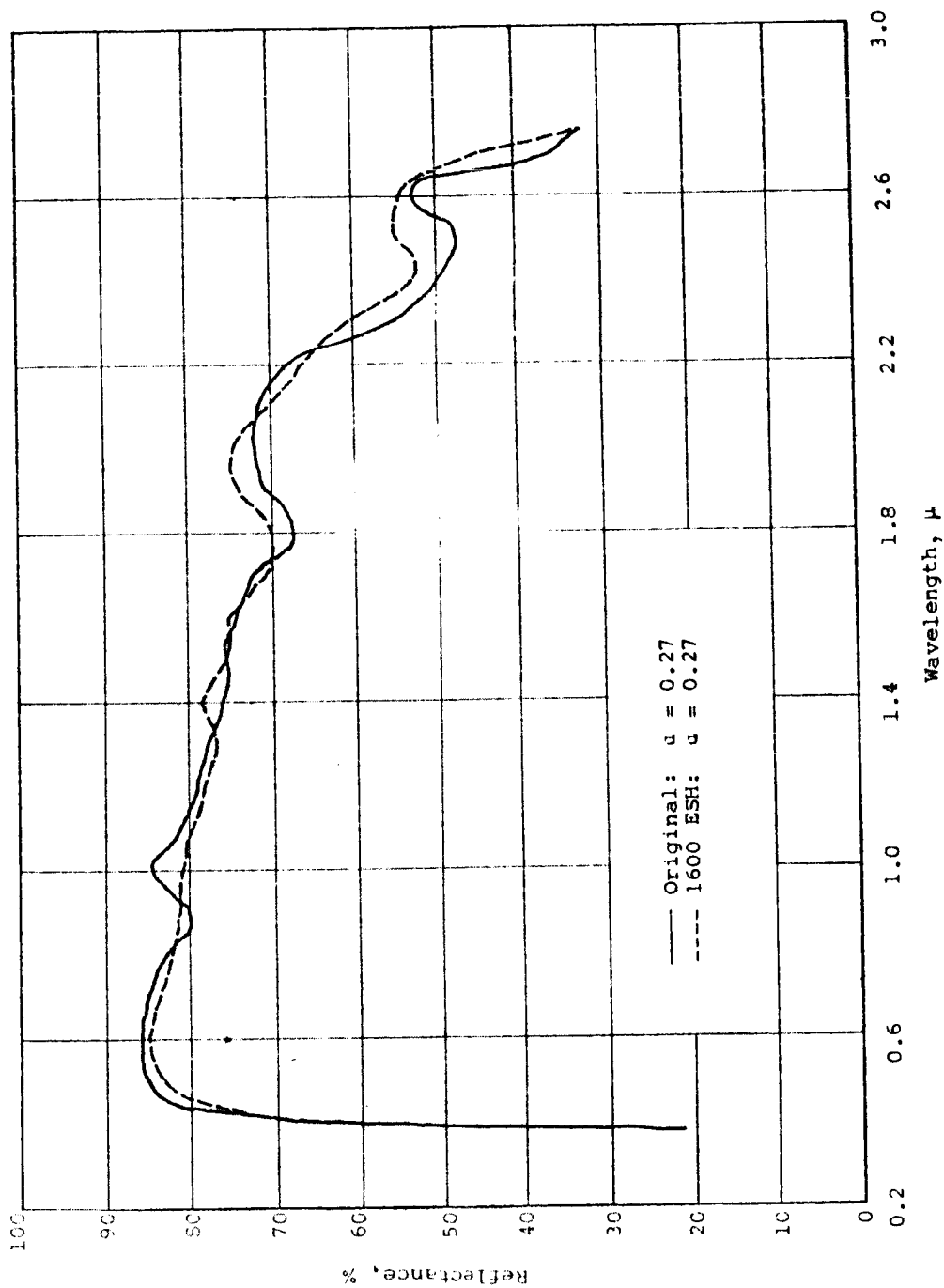


FIGURE 39
 EFFECT OF 1600 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-16

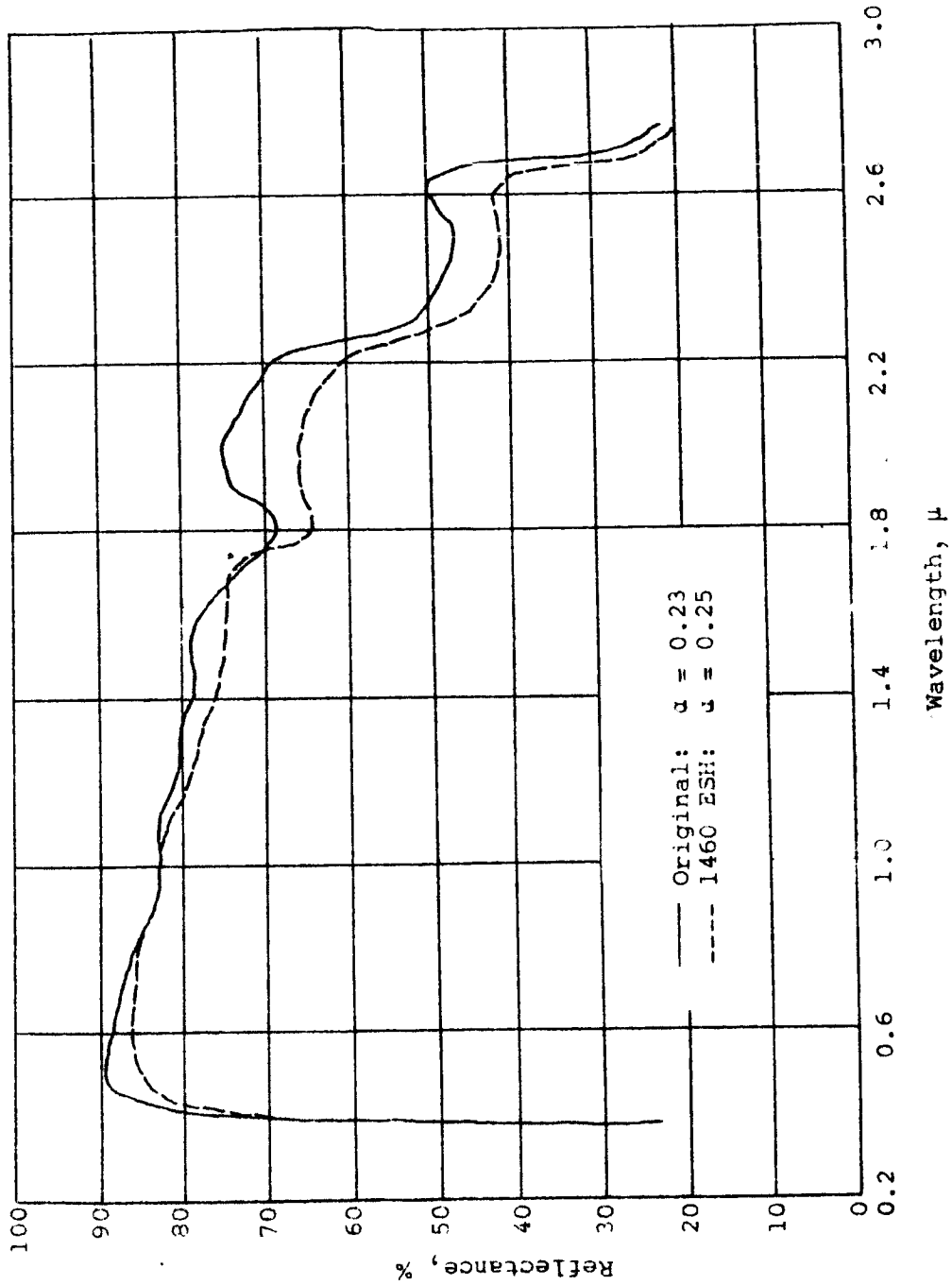


Figure 40
 EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-11

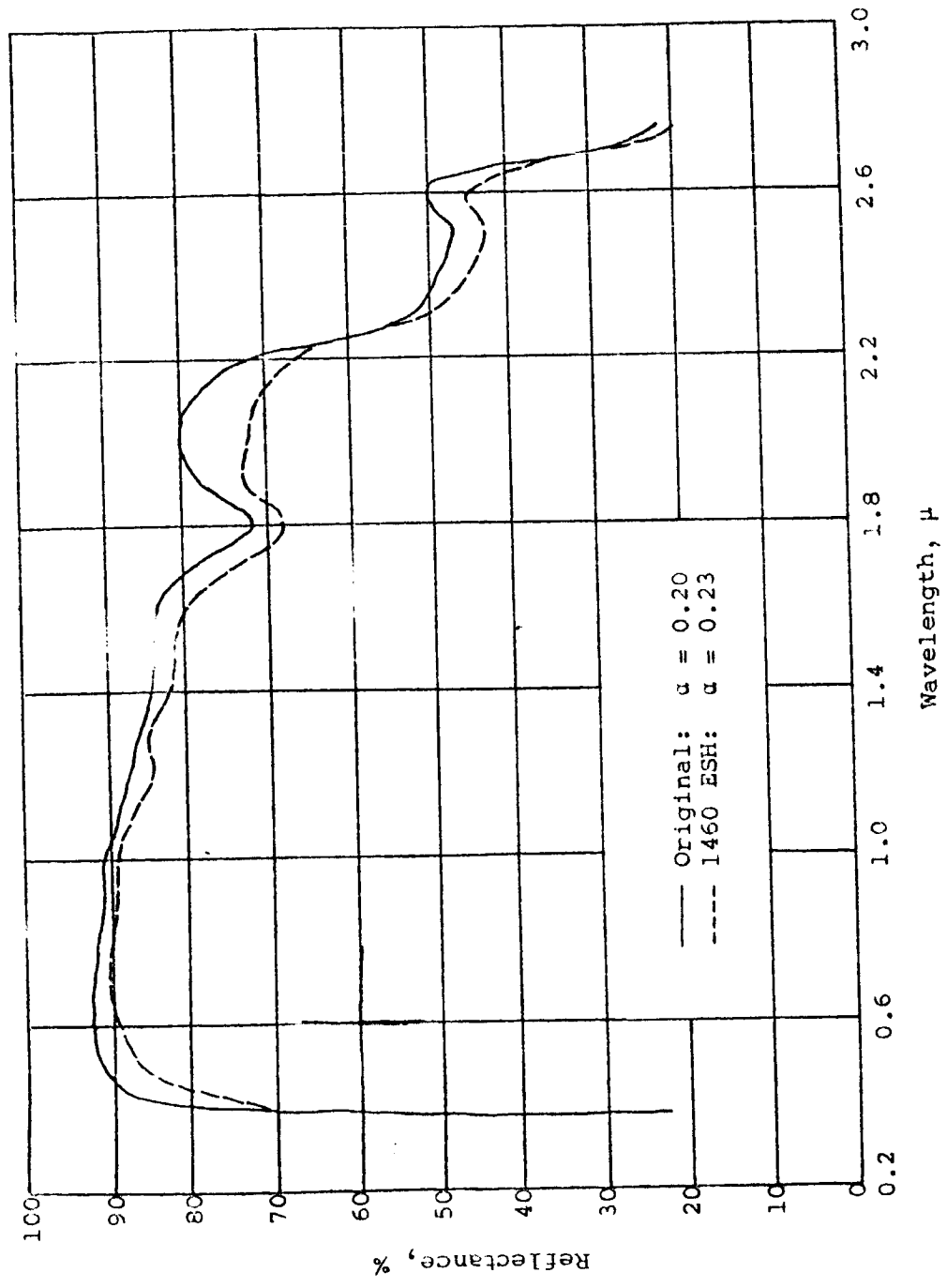


Figure 41
EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-8

Table 26

EFFECT OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF SILICONE PAINTS WITH Me/Si OF 1.33 AND 1.38

| Paint No. | Composition | | Exposure | | Solar Absorbance | | |
|-----------|-------------|--------|----------|--------------|------------------|------|------|
| | Binder | PVC, % | ESH | Solar Factor | 1 | 2 | 3 |
| S-16 | R-7 | 25 | 0 | 8.9 | .139 | .120 | .259 |
| | | | 615 | | .144 | .123 | .267 |
| | | | | | | | .008 |
| S-20 | R-7 | 30 | 0 | 11 | .266 | | .008 |
| | | | 1600 | | .274 | | |
| | | | | | | | |
| S-11 | R-5 | 25 | 0 | 10.7 | .250 | | .010 |
| | | | 1700 | | .260 | | |
| | | | | | | | |
| S-15 | R-5 | 30 | 0 | 11 | .259 | | .012 |
| | | | 1600 | | .271 | | |
| | | | | | | | |
| S-19 | R-5 | 35 | 0 | 9 | .230 | | .020 |
| | | | 1460 | | .250 | | |
| | | | | | | | |
| S-21 | R-5 | 35 | 0 | 10.7 | .230 | | .010 |
| | | | 1700 | | .240 | | |
| | | | | | | | |
| S-16 | R-7 | 25 | 0 | 9.1 | .120 | .098 | .218 |
| | | | 630 | | .124 | .094 | .218 |
| | | | | | | | .000 |
| S-11 | R-5 | 25 | 0 | 8.7 | .125 | .099 | .224 |
| | | | 1200 | | .126 | .100 | .226 |
| | | | | | | | .002 |
| S-15 | R-5 | 30 | 0 | 10.1 | .124 | .099 | .223 |
| | | | 1850 | | .132 | .105 | .237 |
| | | | | | | | .014 |
| S-19 | R-5 | 35 | 0 | 9.6 | .135 | .086 | .221 |
| | | | 660 | | .140 | .086 | .225 |
| | | | | | | | .005 |

(1:1:SP 500:E-F 414)

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Included in Table 26 are the changes in solar absorptance for S-21, which was formulated identically to S-19 except that half the SP 500 zinc oxide was replaced with Eagle-Picher's 414 zinc oxide. A change of 0.005 occurred after exposure to 660 ESH. This test was the only one in the silicone series which used a zinc oxide other than SP 500. The results confirm the earlier findings in the work on the inorganic coatings, namely, that zinc oxide pigments are the most stable class of pigments.

The spectral reflectance of S-19 before and after exposure to both 1200 and 1800 ESH is shown in Figure 42.

4. LTV-602 Paints and Effect of PVC

Paints were formulated from General Electric's LTV-602 polymer at 20, 25, 30, 35, and 40% PVC in order to determine the effect of pigment concentration on stability to a simulated space environment. Experimental resin R-5 was also pigmented at different PVCs. The results of exposure to a simulated space environment are presented in Table 27. The data for the LTV-602 paints show the dependence of stability on PVC. Coating S-7 at 20% PVC showed an increase in solar absorptance of 0.040 compared with 0.030-0.038 for S-13 at 30% PVC and only 0.012 for S-26 at 40% PVC. Similarly, coating S-19 at 35% PVC exhibited a comparatively smaller increase in solar absorptance than either S-11 or S-15 at 25 and 30% PVC, respectively.

The data on LTV-602 in Table 27 are plotted in Figure 43 to show the inverse relation of solarization to PVC. The dependence of stability on PVC is more easily discerned in less stable systems, such as those based on zinc sulfide- or rutile-pigmented methyl-phenyl silicones.¹¹ The zinc oxide-methyl silicone and the zinc oxide-silicate systems are, by virtue of their stability, more susceptible to differences caused by soiling, measurement errors, etc. The spectral reflectance curves of the LTV-602 paints at different PVCs are given before and after exposure in Figures 44 through 48.

In summary, the stability of the zinc oxide-methyl silicone paints is directly proportional to the PVC. This correlation is less well defined in highly stable systems, which are susceptible to soiling, measurement, or simulation discrepancies. LTV-602-based paints, while stable, are more susceptible to damage by ultraviolet irradiation in vacuum than are paints based on the experimental resins of lower Me/Si.

¹¹ Zerlaut, G. A., "Pigment-Binder Relationships in Ultraviolet Irradiated Paints in Vacuum," Preprints, Division of Organic Coatings and Plastics Chemistry, 40th National Meeting American Chemical Society, Chicago, Sept. 1961.

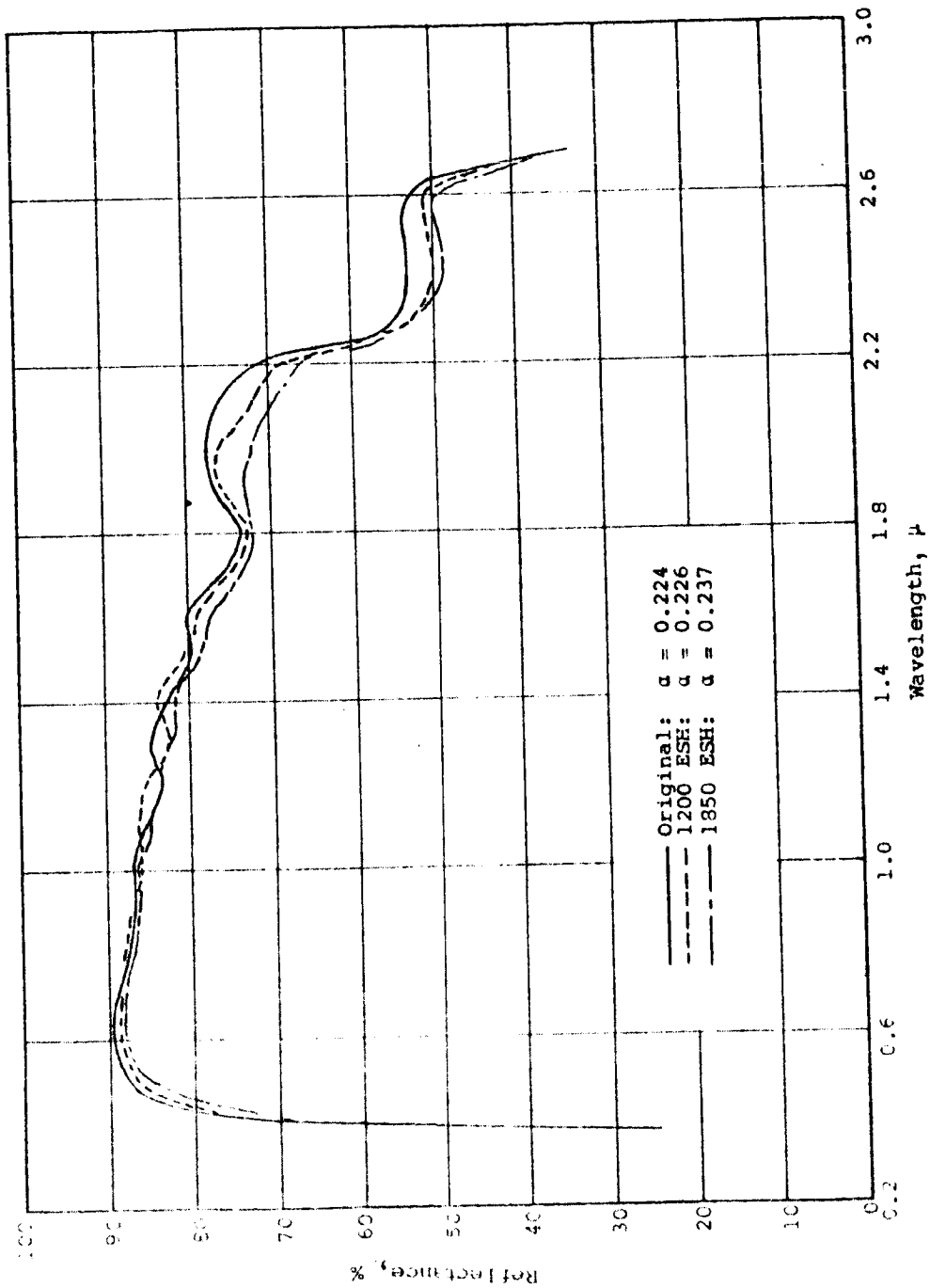


Figure 42
EFFECT OF 1200 AND 1850 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-19

Table 27

EFFECT OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF SILICONE PAINTS AS A FUNCTION OF PVC

| Paint No. | Composition | | Exposure | | Solar Absorbance | | | |
|-----------|-------------|--------|----------|--------------|------------------|----------------|------|------|
| | Binder | PVC, % | ESH | Solar Factor | a ₁ | a ₂ | a | Δa |
| S-7 | LTV-602 | 20 | 0 | 9 | | | .220 | |
| | | | 1460 | | | | .260 | .040 |
| | | | 0 | 17.6 | | | .240 | |
| | | | 3350 | | | | .300 | .060 |
| S-12 | LTV-602 | 25 | 0 | 9 | | | .230 | |
| | | | 1460 | | | | .260 | .030 |
| S-13 | LTV-602 | 30 | 0 | 9 | | | .230 | |
| | | | 1460 | | | | .260 | .030 |
| | | | 0 | 8.7 | .115 | .087 | .202 | |
| | | | 1200 | | .141 | .099 | .240 | .038 |
| | | | 0 | 17.6 | | | .230 | |
| | | | 3350 | | | | .280 | .050 |
| S-27 | LTV-602 | 35 | 0 | 10.2 | | | .175 | |
| | | | 1600 | | .107 | .068 | .192 | .017 |
| | | | 0 | 10.1 | .106 | .071 | .176 | |
| | | | 1850 | | .120 | .081 | .201 | .025 |
| S-26 | LTV-602 | 40 | 0 | 8.7 | | | .161 | |
| | | | 1200 | | .105 | .056 | .173 | .012 |
| S-11 | R-5 | 25 | 0 | 9 | | | .230 | |
| | | | 1460 | | | | .250 | .020 |
| S-15 | R-5 | 30 | 0 | 10.7 | | | .230 | |
| | | | 1700 | | | | .240 | .010 |
| S-19 | R-5 | 35 | 0 | 8.7 | | | .224 | |
| | | | 1200 | | .125 | .099 | .226 | .002 |
| | | | 0 | 10.1 | .124 | .099 | .223 | |
| | | | 1850 | | .132 | .105 | .237 | .014 |

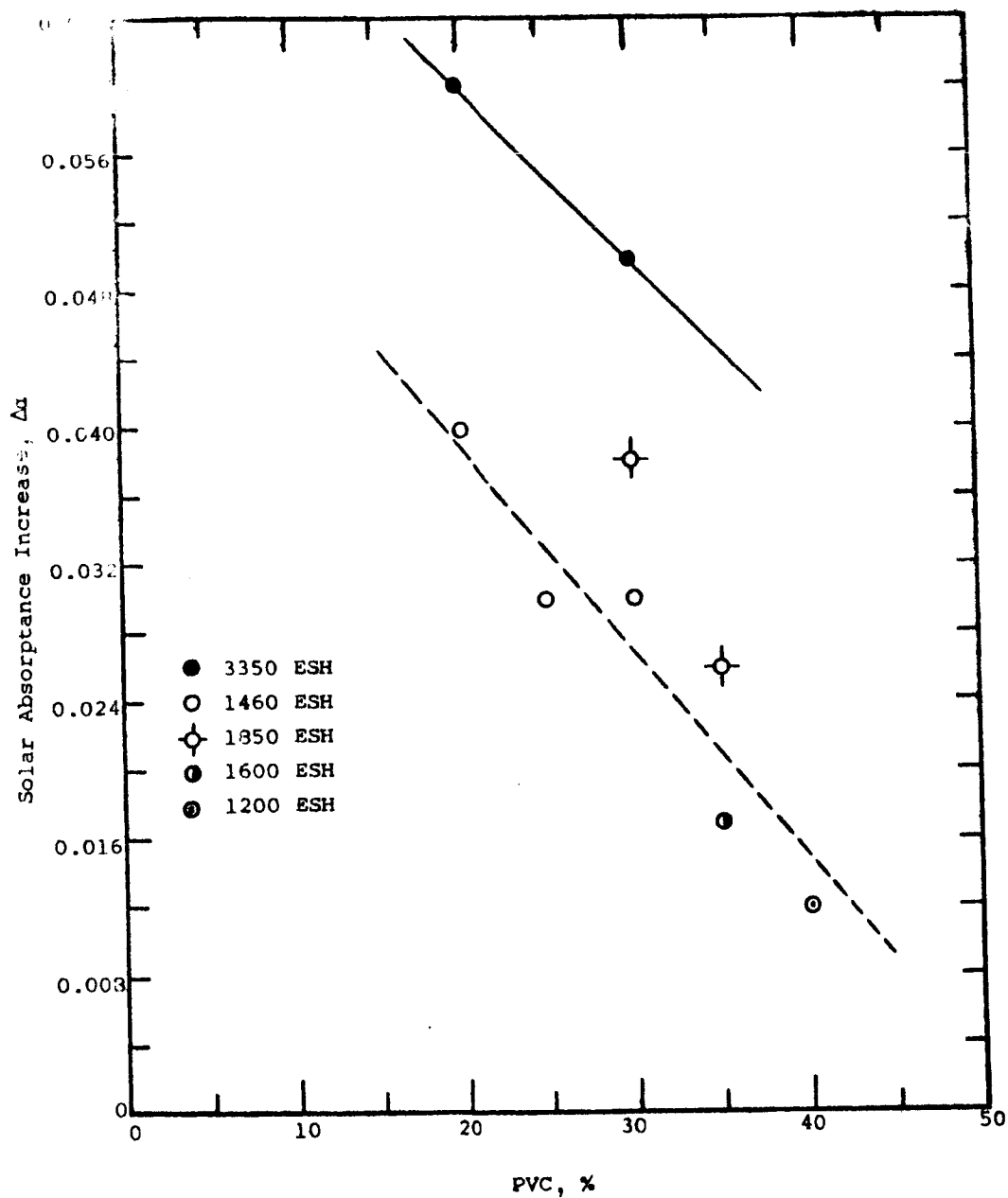


Figure 43
SOLAR ABSORPTANCE VERSUS PVC IN LTV-602 PAINTS

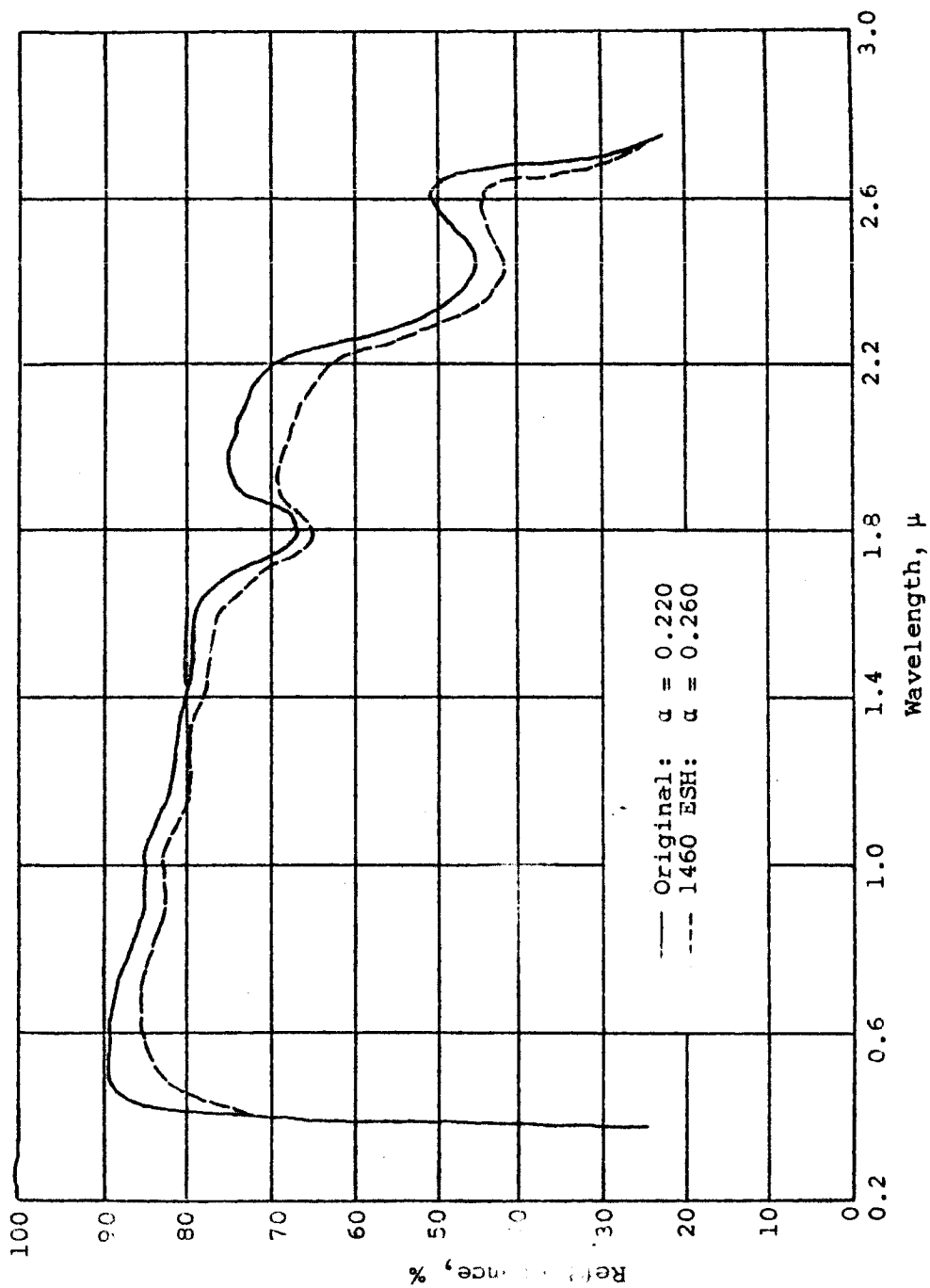


Figure 44
EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-7

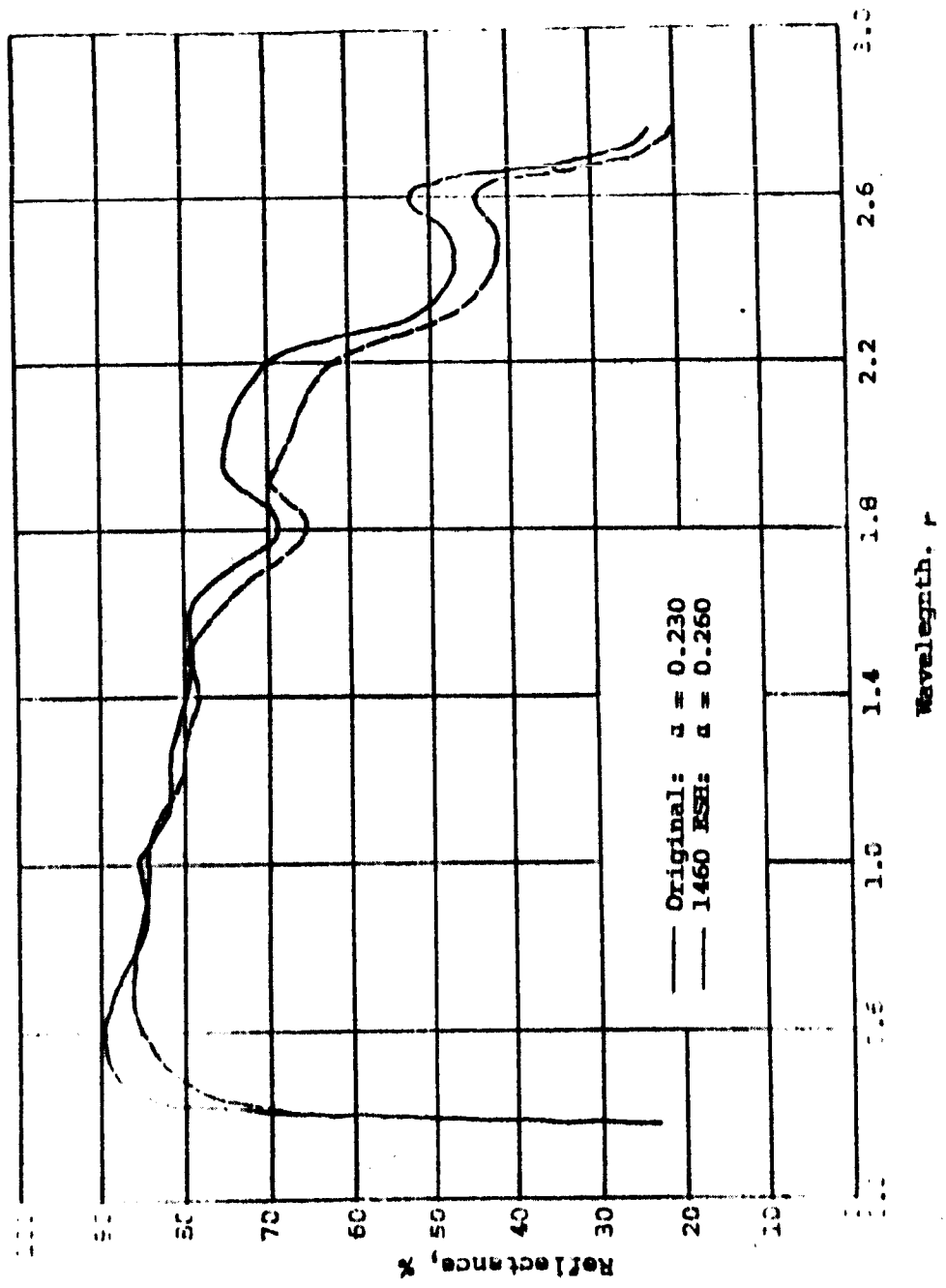


Figure 45

EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-12

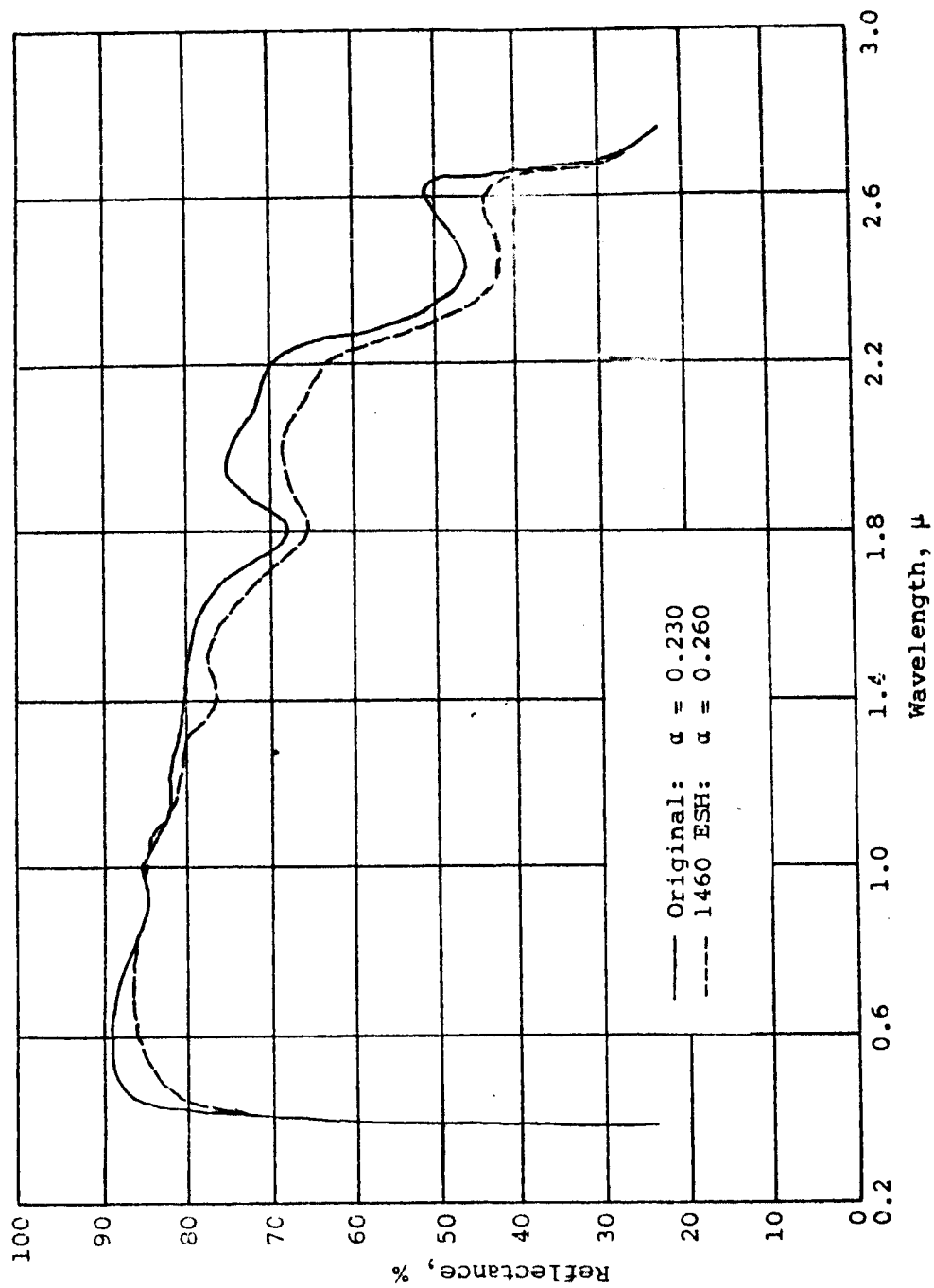


Figure 46
EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-13

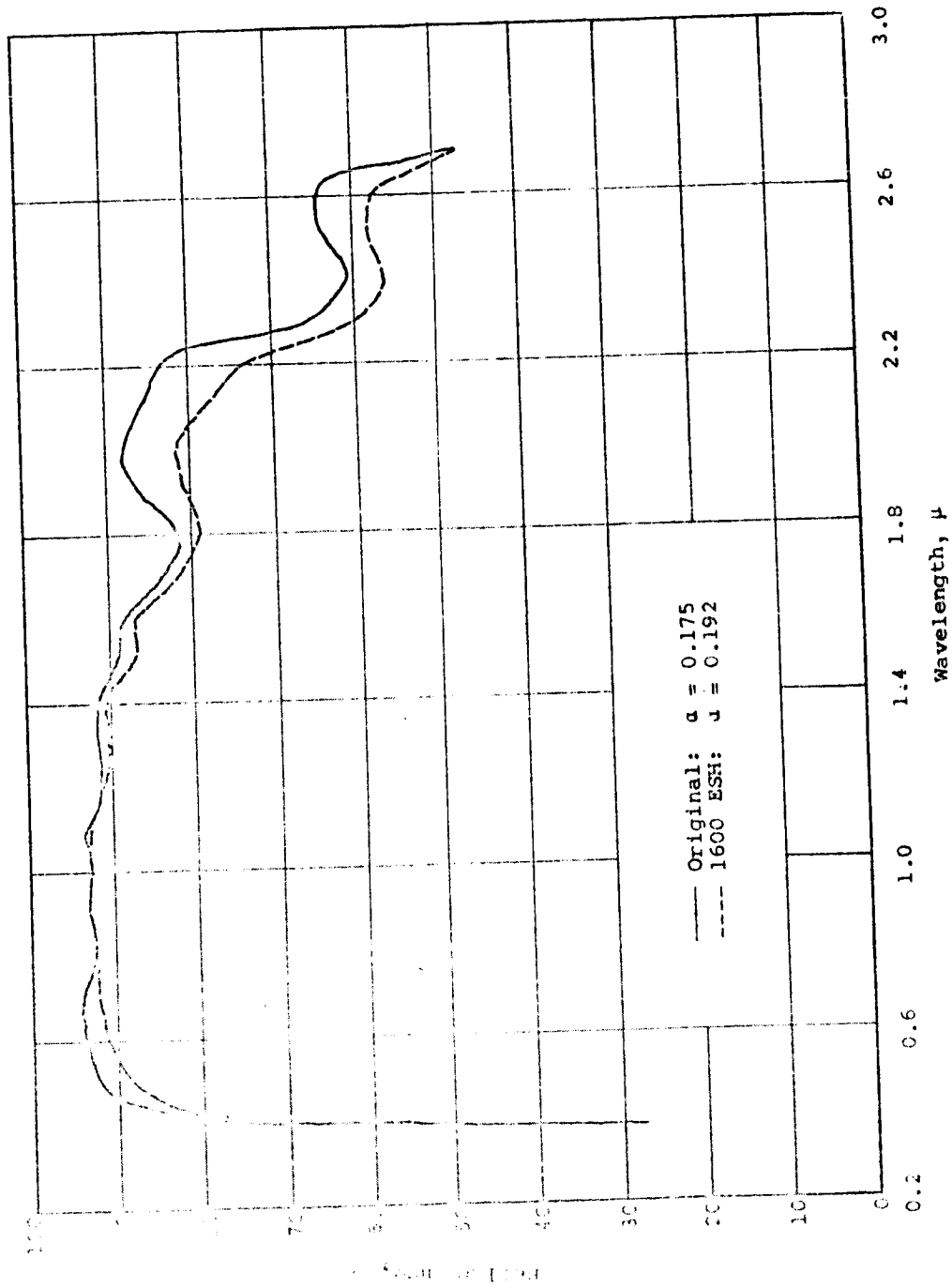


Figure 47
 EFFECT OF 1600 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT 3-27

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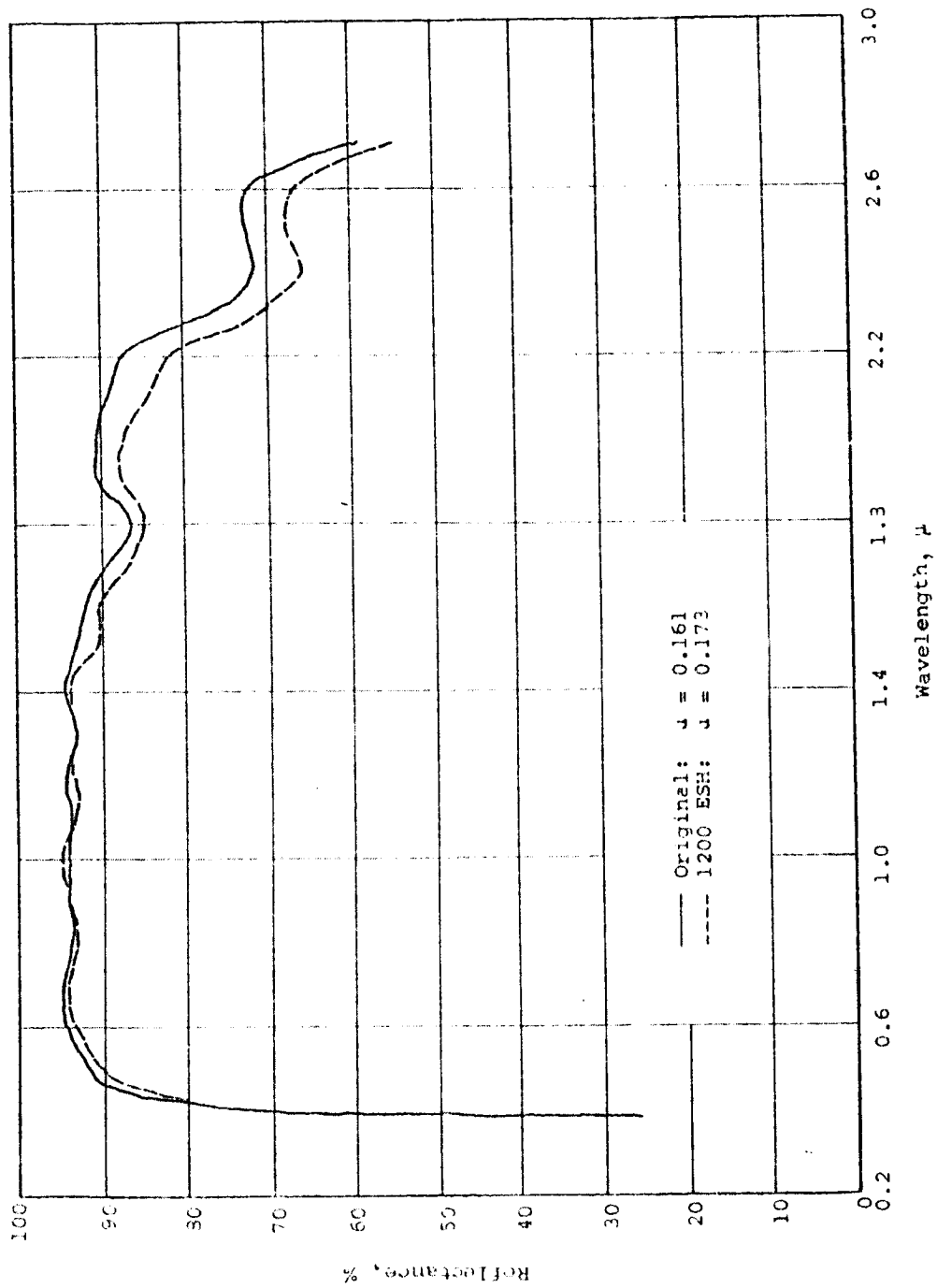


Figure 48
EFFECT OF 1200 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF S-26

5. Effects of Soiling and Cleaning

The effects of various treatments on the ultraviolet stability of three methyl silicone paints are presented in Table 28. Soiling was accomplished by "rubbing" Duo Seal vacuum-pump oil into the surface. The surfaces were then cleaned with either acetone-moistened facial tissue or lathered Lava soap, followed by copious amounts of tap water and a 72-hour period of air-drying. Several specimens of S-7 were treated by heating in a forced-air oven for 3 hours at 400°F. A specimen of S-7 and one of S-8 were thermally shocked for 10 cycles at 200 to -200°F in about 3 minutes.

Soiling and cleaning had little effect on reflectance or ultraviolet stability. The only exception was S-7, which showed a 6.0% loss in reflectance at 440 mμ after soiling. This loss might be attributable in part to the affinity of the elastomeric methyl silicone paint for dirt. Because of this natural soiling problem and the length of time between preparation and exposure it was necessary to clean the S-7 specimens before their initial reflectances were measured. This problem was considerably less acute with LTV-602 paint S-13 pigmented at 30% PVC, and was nonexistent with S-27 and S-26 pigmented at PVCs of 35 and 40%, respectively. Coatings S-4 and S-8, which contained methyl silicone resins rather than the elastomeric LTV-602, did not require washing prior to irradiation except for the deliberately soiled specimens. The effect of thermal shocking on stability could not be ascertained from the data.

The results of subsequent space simulation tests emphasized the undesirability of using acetone as a cleansing agent for space-stable coatings. On several occasions the edges or corners of specimens were inadvertently contaminated with sebum from fingerprints and were deliberately washed with acetone. Any photolysis which occurred was confined to the outermost edges and corners outside the reflectometer's field of view. Areas "cleaned" with acetone were inconsistently degraded, whereas those soiled with fingerprints were always photolyzed. As a result of these experiments, the only method of cleansing used thereafter consisted of washing with detergent and copious quantities of water.

6. Paints Based on Distilled Resins

It was previously noted that zinc oxide paints based on undistilled methyl resins (e.g. R-5) undergo optical flattening and an increase in porosity upon curing. Even though this process may involve thermal erosion on the surface of the organic portion of the resin, the cured films were very stable to the simulated space environment (see Table 26), but their

Table 28

COMBINED EFFECTS OF SOILING AND CLEANING AND OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF SILICONE PAINTS

| Paint No. | Binder | Composition | | Heated | Soiled | Treatment | | Exposure ESH | Solar Factor | Reflectance, % | |
|-----------|---------|-------------|---|--------|--------|--------------------------|----------------------------|-----------------|-----------------|----------------|-------------|
| | | PVC, % | Cure | | | Cleaned with Water | Cleaned with Acetone | | | 440 m μ | 600 m μ |
| S-4 | R-1 | 25 | 24 hr at room temp. + 16 hr at 300°F | | | | | 0 | | 82.2 | 86.0 |
| | | | | | | | | 250 | 2.7 | 80.2 | 86.4 |
| | | | | | X | X | | 0 | | 82.6 | 87.6 |
| | | | | | | | | 270 | 3 | 80.7 | 87.6 |
| | | | | | X | | X | 0 | | 81.8 | 84.6 |
| | | | | | | | | 270 | 3 | 80.0 | 85.0 |
| S-7 | LTV-602 | 20 | 72 hr at room temp. | | | | X | 0 | | 88.7 | 92.9 |
| | | | | | | | | 270 | 3 | 86.7 | 92.6 |
| | | | | X | X | X | | 0 | | 79.5 | 90.3 |
| | | | | | | | | 250 | 2.7 | 73.5 | 88.1 |
| | | | | X | | | X | 0 | | 79.4 | 90.3 |
| | | | | | | | | 250 | 2.7 | 75.6 | 89.0 |
| | | | | X | | | X | 0 | | 78.9 | 91.0 |
| | | | | | | | | 250 | 2.7 | 74.5 | 89.0 |
| S-8 | | | 4 hr at room temp. + 16 hr at 300°F | | | | | 0 | | 83.8 | 89.4 |
| | | | | | | | | 250 | 2.7 | 83.5 | 89.3 |
| | | | | | X | | X | 0 | | 84.0 | 88.6 |
| | | | | | | | | 250 | 2.7 | 83.0 | 89.0 |
| | | | | | X | X | | 0 | | 83.5 | 89.5 |
| | | | | | | | | 250 | 2.7 | 81.5 | 90.0 |
| | | | | | | | | 0 | | 83.5 | 90.5 |
| | | | | | | | X | 270 | 3 | 82.0 | 90.4 |

porosity and their 300°F curing requirement provide no advantages over the porous potassium silicate paints. It was this porosity and the resultant susceptibility to soiling which prompted molecular distillation experiments with resin R-5. These experiments were aimed at the production of higher-molecular-weight resins in the hope that paints based on them would produce glossy more soil-resistant and easily cleanable coatings.

The effects of ultraviolet irradiation in vacuum on the paints based on molecularly distilled resins are presented in Table 29. Paint S-22 prepared from the higher-boiling fraction of R-5 degraded the most severely of all coatings in this group. It is suspected that this degradation was due in part to the use of zinc octoate catalyst (Silicure Z-775), since paint S-25 which did not degrade as severely was formulated from the same resin but was cured with tetrabutoxy titanium. Additional evidence that zinc octoate might be detrimental to stability was provided by the results of irradiation of S-23 (cured with tetrabutoxy titanium) in comparison with irradiation of S-24 (cured with Z-775). Paints S-23 and S-24 were prepared from the lower-boiling fraction of R-5. This fraction was redistilled and designated R-5B. These paints optically flattened and became somewhat porous similarly to paints formulated from the parent resin, R-5.

Paints S-29 and S-31 both showed good stability and remained bright and glossy during the tests. These paints have the appearance of "refrigerator enamel" and are exceptionally soil-resistant. The effect of cure on the stability of S-31 is shown in Table 29. The specimen which was heated for 1 hour at 500°F in addition to the standard 1-hour cure at 300°F underwent less than a third the degradation experienced by the untreated (nonheated) specimen. After an exposure to 1780 ESH the unheated specimen underwent an 0.020 increase in solar absorptance while the specimen heated to 500°F underwent an increase of only 0.006. The reflectance curves for these two paints are presented in Figures 49 and 50.

In summary, paints formulated from methyl silicone polymers upgraded by molecular distillation possess excellent gloss, soil resistance and cleanability. These resins based on a stock polymer with an Me/Si of 1.38 possess stabilities intermediate between paints based on the stock R-5 resin and those based upon the elastomeric LTV-602 polymer.

Table 29

EFFECT OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF ZINC OXIDE-PIGMENTED PAINTS
BASED ON MOLECULARLY FILLED EXPERIMENTAL METHYL SILICONE RESINS

| Paint No. | Composition | | Exposure | | Solar Absorbance | | | |
|-----------|----------------------|--------|-----------|--------------|------------------|----------------|--------------|------|
| | Binder | PVC, % | ESH | Solar Factor | a ₁ | a ₂ | a | Δa |
| S-22 | R-5A | 35 | 0 620 | 9 | .125 .143 | .101 .102 | .225 .245 | .019 |
| S-23 | R-5B | 35 | 0 1140 | 8.3 | .127 .132 | .108 .111 | .235 .243 | .008 |
| S-24 | R-5B | 35 | 0 1140 | 10.1 | .128 .135 | .108 .114 | .236 .249 | .013 |
| S-25 | R-5A | 35 | 0 1580 | 8.3 | .133 .139 | .115 .124 | .248 .263 | .015 |
| S-29 | R-8 | 35 | 0 1000 | 11.4 | .141 .144 | .139 .142 | .280 .286 | .006 |
| S-31 | R-8 | 40 | 0 1600 | 14.2 | .137 .145 | .132 .138 | .269 .283 | .014 |
| | | | 0 1850 | 10.1 | .151 .161 | .148 .154 | .299 .315 | .016 |
| | | | 0 1600 | 10.5 | .128 .136 | .125 .130 | .253 .266 | .013 |
| | | | 0 1780 | 10.2 | .125 .130 | .117 .126 | .241 .257 | .016 |
| | | | 0 1600 | 9 | .132 .139 | .129 .138 | .261 .277 | .016 |
| | | | 0 1780 | 9.4 | .134 .146 | .131 .139 | .265 .285 | .020 |
| | Heated 1 hr at 500°F | | 0 1780 | 9.4 | .134 .136 | .126 .130 | .260 .266 | .006 |

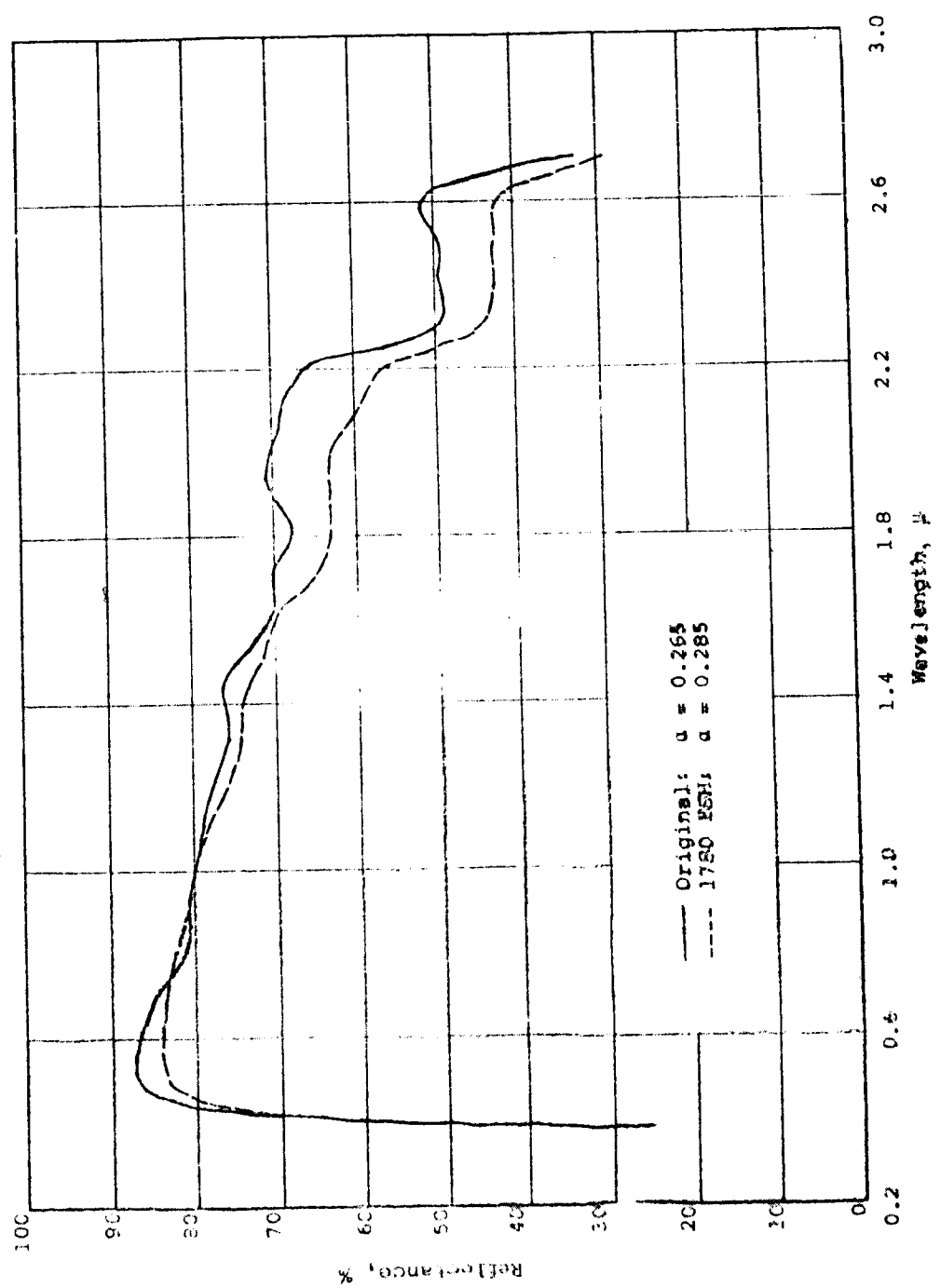


Figure 49
 EFFECT OF 1780 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-31

63-552

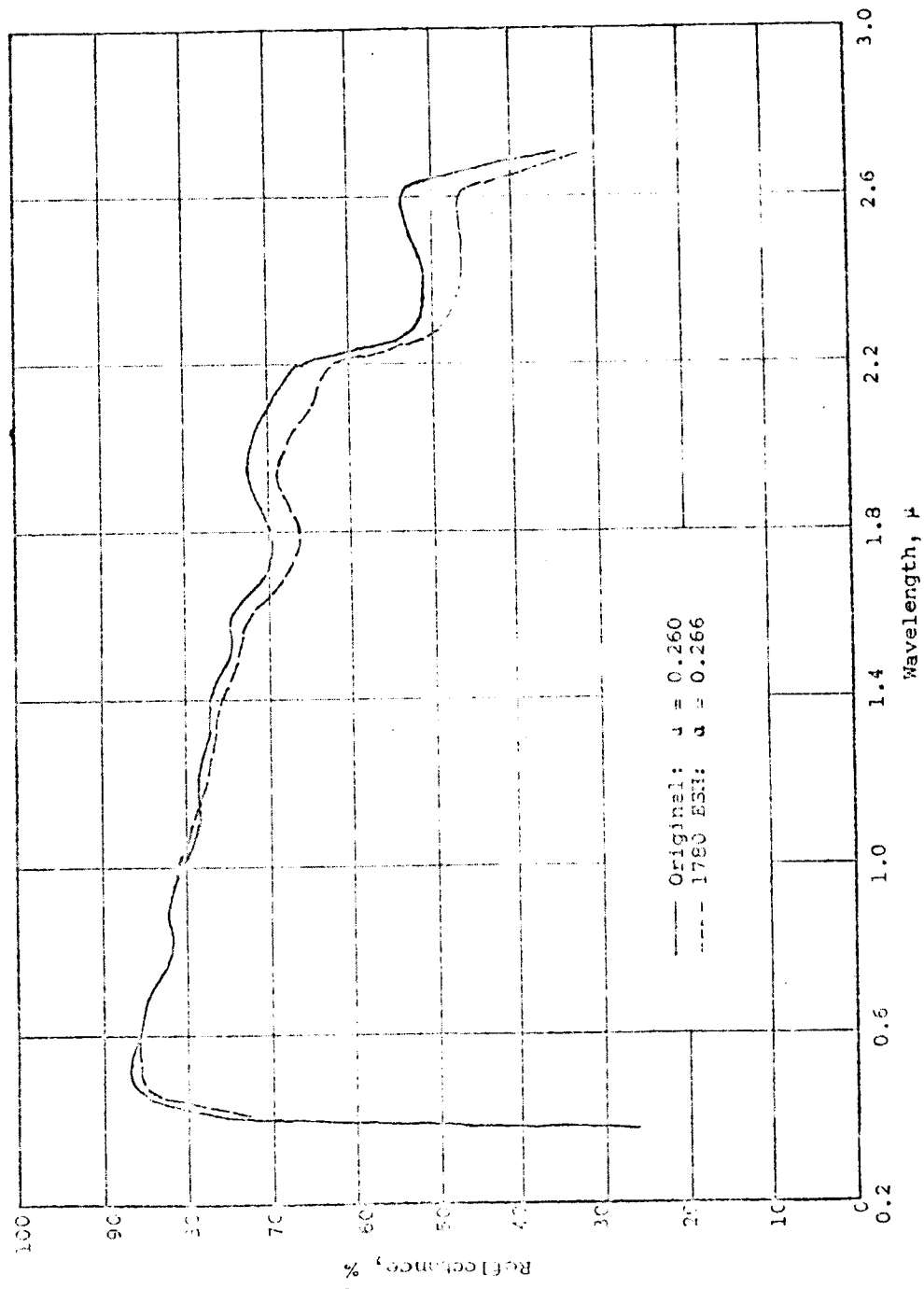


Figure 50
EFFECT OF 1780 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-31
HEATED FOR 1 HOUR AT 500°F

7. Miscellaneous Silicone Paints

The results of exposure of several miscellaneous silicone paints are presented in Table 30. Paint S-17 was formulated from Dow Corning's 808 methyl-phenyl resin pigmented with Titanox RA-NC, a nonchalking rutile titanium dioxide. This paint was formulated for the Round Robin Testing Program and is included here for purposes of comparison.

S-18 and S-30 were based on General Electric's SR-80 and 81932 resins, respectively. SR-80 was reported to be a purely methyl silicone resin containing zinc octoate catalyst. Unlike the other methyl silicone resins studied, however, the zinc oxide paint (S-18) made from SR-80 degraded severely after exposure to only 1600 ESH. It increased 40% in solar absorptance. These disappointing results were attributed to the zinc octoate catalyst. So 81932 resin was then obtained. The 81932 resin was reported to be identical to SR-80 except that it did not contain zinc octoate catalyst. Paint S-30 was formulated from the 81932 resin and was subsequently found to degrade even more severely than S-18, increasing 54% in solar absorptance after only 1600 ESH. Therefore, we concluded that the resins were not purely methyl silicones. Infrared transmission analyses of these resins did not show typical methyl-phenyl structure nor did their absorption spectra match polydimethylsiloxane spectra. The absorption spectra of SR-80 and 81932 are identical and have not yet been interpreted.

Coatings S-28 and S-32 were formulated for the purpose of determining the degree of stability of rutile paints. The results of exposure to ultraviolet in vacuum showed the necessity for pigment-vehicle combinations formulated from materials which are separately stable. Figures 51 and 52 show the reflectance changes of these two paints.

S-32 was pigmented with Du Pont's new V. Pure R-900-1. The exceptional reflectance properties of this paint are manifested in the ρ_1 and ρ_2 of only 0.099 and 0.080, respectively. Unfortunately, paints prepared from R-900-1 do not offer any other advantage over those pigmented with a standard rutile, since S-32 increased 67% in solar absorptance after only 1650 ESH. S-32 was periodically examined visually through the quartz window during the space-simulation test and did not appear severely degraded until after 1000 ESH, after which it began to appear gray compared with the adjacent, white zinc oxide paints. Figure 52 indicates the graying by the flat reflectance curve of the degraded specimen over a 1.2- μ spread. In contrast, the standard rutile paints did not gray but yellowed, as evidenced by a severe decrease in reflectance in the blue region around 440-m μ wavelength.

Table 30

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF MISCELLANEOUS SILICONE PAINTS

| Paint No. | Composition | | | PVC, % | ESK Factor | Solar Absorbance | | |
|------------|-------------|--------------------|----|-----------|---------------|------------------|----------------|----------------|
| | Binder | Pigment | | | | w | w ₂ | w ₃ |
| S-17 | 808 TBT | Titanox RA-NC | 45 | 0 | 11 | .296 | | .110 |
| | | | | 1600 | | .406 | | |
| S-18 | SR-30 | SP 500 ZnO | 25 | 0 | 11 | .279 | | .111 |
| | | | | 1600 | | .390 | | |
| S-30 | 31932 | SP 500 ZnO | 25 | 0 | 10.2 | .141 | .142 | .283 |
| | | | | 1600 | | .241 | .192 | .433 |
| S-28 | LTV-602 | Titanox RA-10 | 30 | 0 | 10.1 | .120 | .077 | .197 |
| | | | | 1850 | | .191 | .156 | .347 |
| S-32 | LTV-602 | TiPure R-900-1 | 35 | 0 | 9 | .099 | .080 | .179 |
| | | | | 1650 | | .158 | .140 | .298 |
| ZM-60* | 808 TBT | ZnS | 60 | 0 | 9 | .117 | .127 | .244 |
| | | | | 1250 | | .188 | .126 | .314 |
| ZMO-40* | 808 TBT | SP 500 ZnO | 40 | 0 | 9 | .117 | .104 | .221 |
| | | | | 1250 | | .169 | .112 | .281 |
| Q-9-0107** | Proprietary | r-TiO ₂ | 25 | 0 | 10.7 | .103 | .111 | .214 |
| | | | | 1480 | | .165 | .206 | .371 |
| Q-9-0108** | Proprietary | ZnS | 15 | 0 | 11.1 | .100 | .120 | .220 |
| | | | | 1530 | | .193 | .131 | .324 |
| Q-9-0106** | Proprietary | SP 500 ZnO | 25 | 0 | 10.6 | .116 | .107 | .223 |
| | | | | 1460 | | .140 | .111 | .251 |
| | | | | 1600 | 10.2 | .114 | .099 | .214 |
| | | | | 1850 | 10.1 | .120 | .108 | .228 |
| | | | | | | .144 | .117 | .261 |

* Furnished by JPL.

** Furnished by Dow Corning Corp.

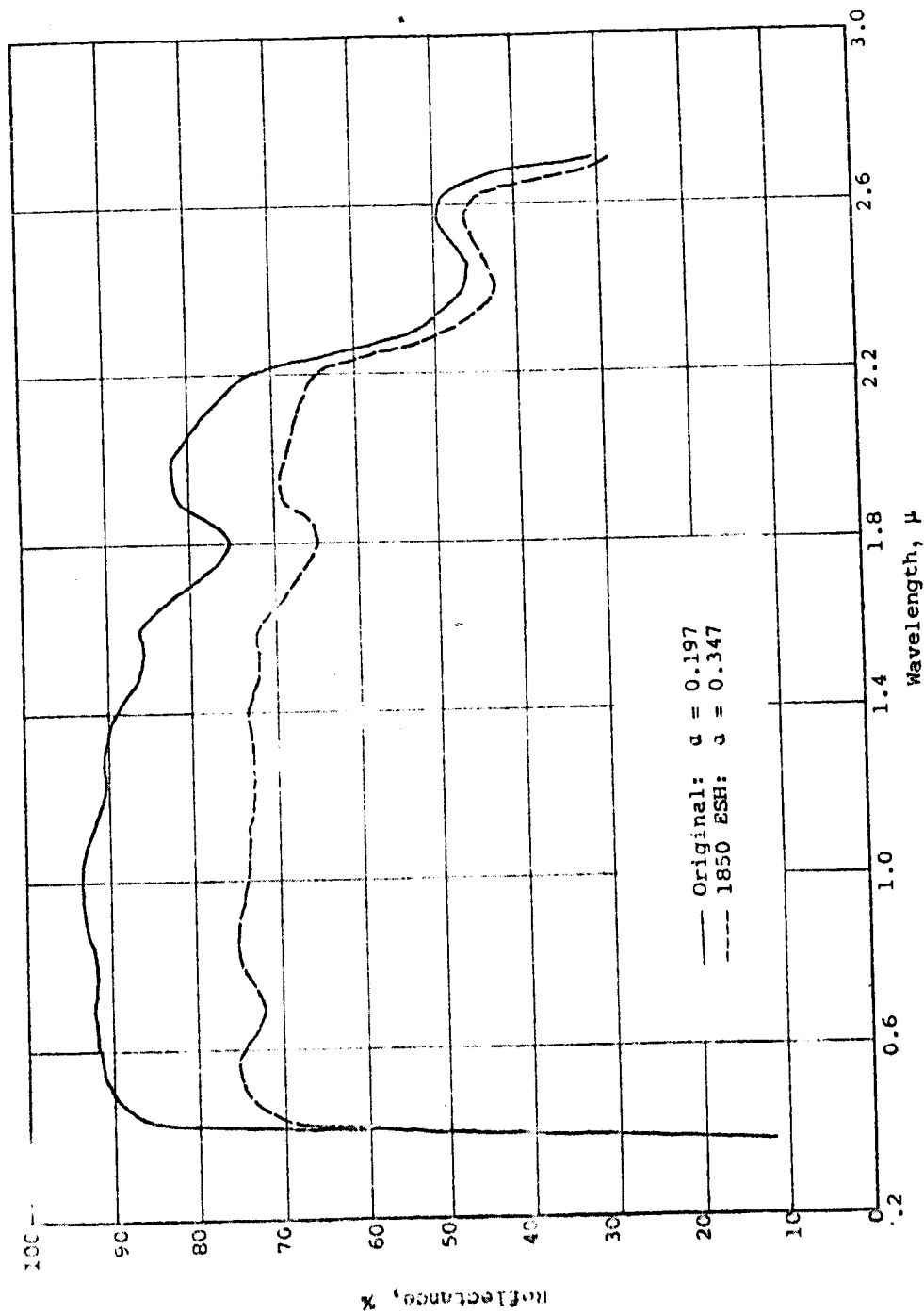


Figure 51
EFFECT OF 1850 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-28,
BASED ON TITANOX RA-10

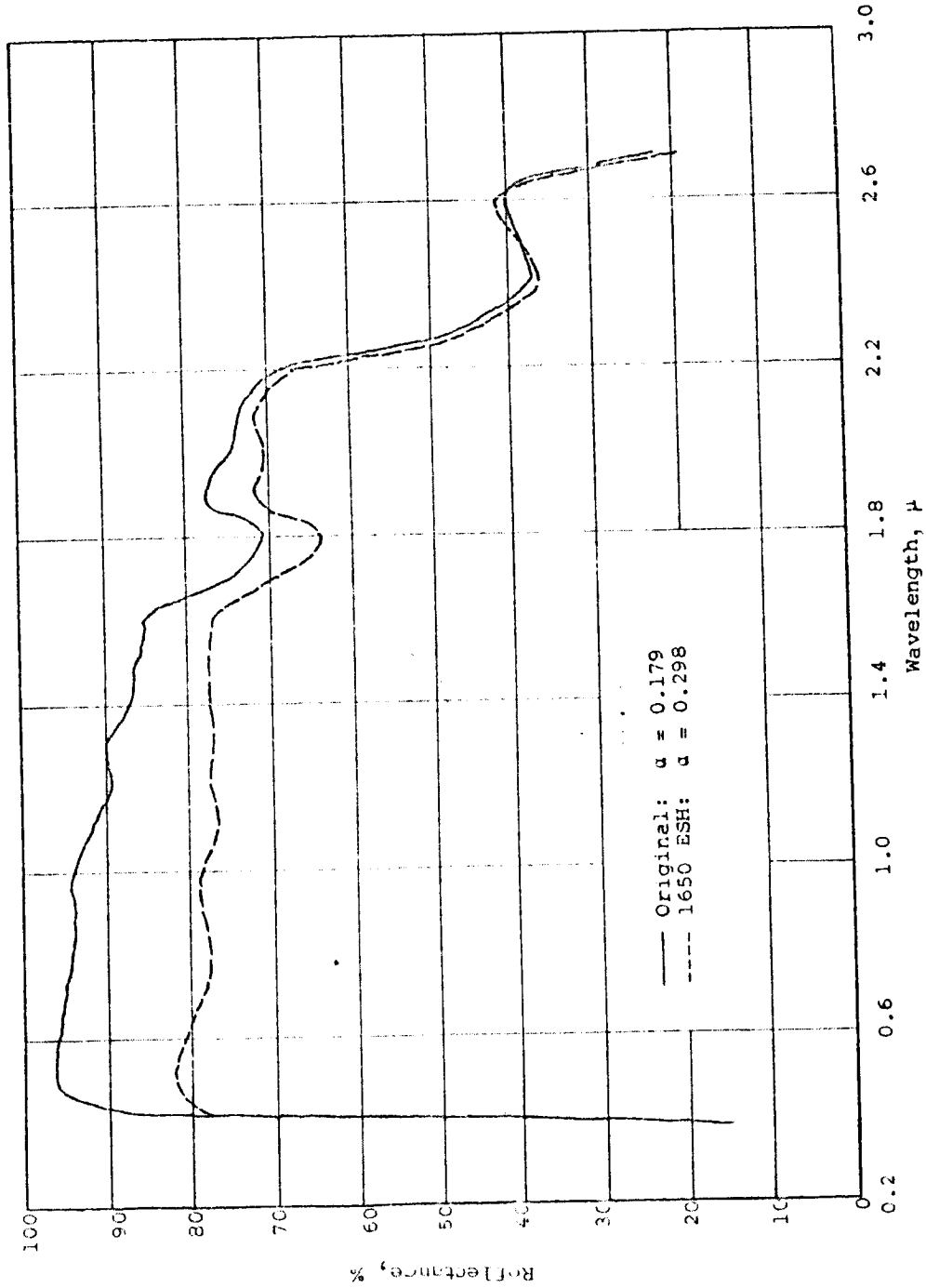


Figure 52

EFFECT OF 1650 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT S-32,
BASED ON TITANE R-900-1 RUTILE

Paints ZW-60 and ZNO-40 were furnished by the Jet Propulsion Laboratory. ZW-60 was pigmented with zinc sulfide at 60% PVC, a value which probably exceeds the critical PVC. ZNO-40 was pigmented with SP 500 zinc oxide at 40% PVC. Both paints were based upon Dow Corning's 808 methyl-phenyl silicone resin. The results of exposure to 1250 ESH show that zinc sulfide was less effective than zinc oxide but superior to rutile in protecting the vehicle from ultraviolet radiation (compare results for S-17 in Table 30). This was not surprising in light of work reported previously.^{11,12} The 0.06 (27%) increase in the solar absorptance of ZNO-40 again emphasizes the difference between phenyl-containing and purely methyl silicone vehicles. The reflectance curves of ZW-60 and ZNO-40 are presented in Figures 53 and 54, respectively.

Coating Q-9-0106 was formulated by Dow Corning Corporation at our request. Dow Corning's Q-9-0106, Q-9-0107, and Q-9-0108 are all based on a proprietary methyl silicone RTV elastomer and are pigmented with SP 500 zinc oxide, rutile titanium dioxide, and zinc sulfide, respectively. All three coatings air-dried overnight to adherent, soft, resilient films. The large increase in the solar absorptance of Q-9-0108 was attributed in part to the low PVC. The change in solar absorptance of Q-9-0107 agreed closely with that of S-28, also a rutile-pigmented methyl elastomer. Q-9-0106 compared favorably with S-13 in resistance to degradation, although S-13 was tougher and less easily scratched or gouged. However, Q-9-0106 appeared to possess less affinity for dirt than S-13.

The reflectance changes of the three Q-series paints are presented in Figures 55, 56, 57. The reflectance increase in the near-infrared which occurs in zinc sulfide-pigmented paints was less pronounced in Q-9-0108 (Figure 57) than in ZW-60 (Figure 53). This phenomenon has also been reported by Cowling et al.¹²

8 4170-ESH Test (No. 23)

The results of exposure of four zinc oxide-pigmented methyl silicone paints to 4170 ESH of ultraviolet radiation in vacuum are presented in Table 31. This was the longest exposure to a simulated space environment of the entire program and amounts to nearly a half year of 100% normal sunlight.

¹² Cowling, J. E. et al., "The Design of Organic Coatings For Use in the Space Environment," Proceedings Coatings for the Aerospace Environment, Report WADD-TR-60-733, Nov 9-10, 1960

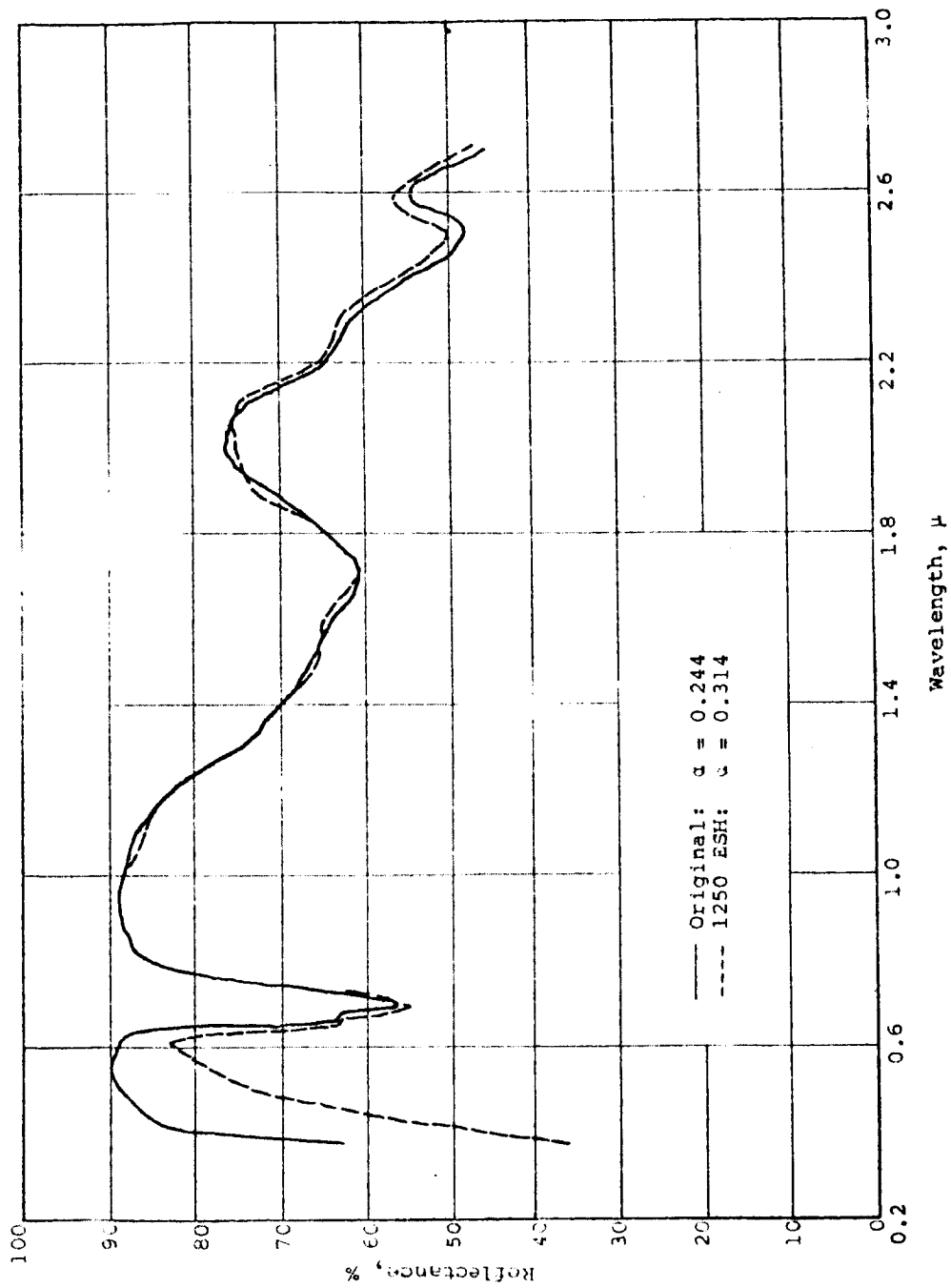


Figure 53

EFFECT OF 1250 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT ZW-60
(FURNISHED BY JFL)

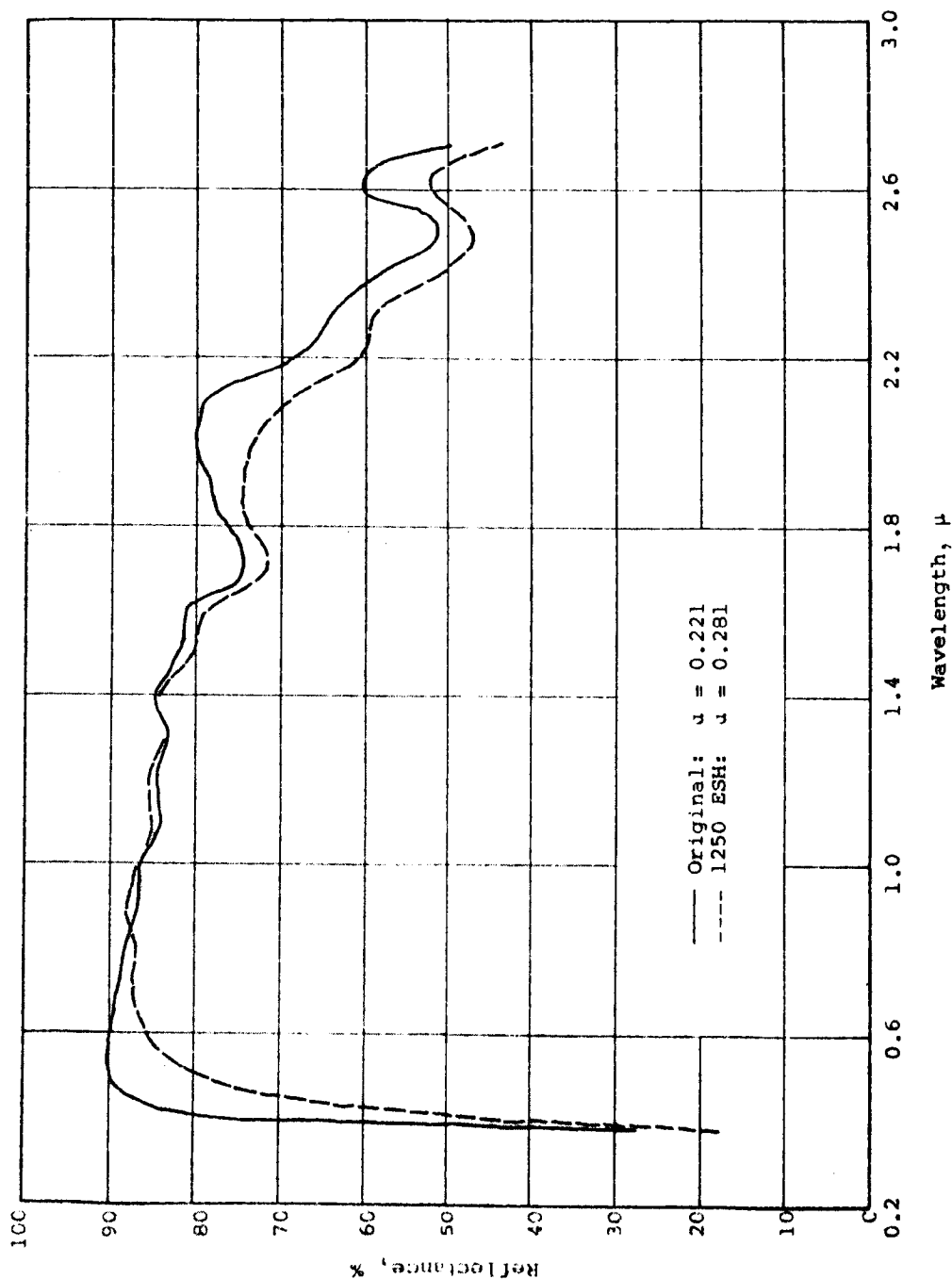


Figure 54
 EFFECT OF 1250 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT ZNO-40
 (FURNISHED BY JPL)

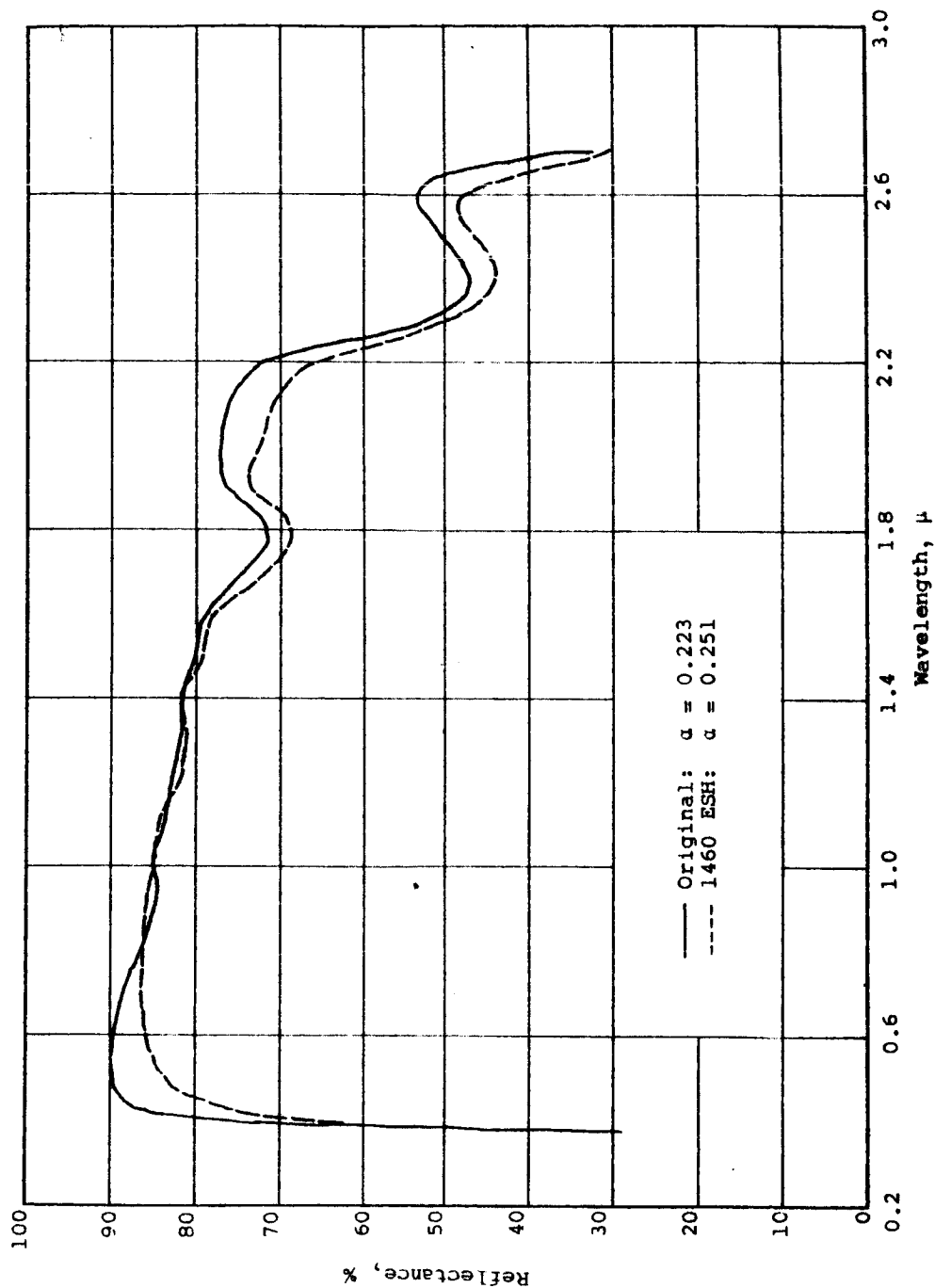


Figure 55

EFFECT OF 1460 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT Q-9-0106
(FURNISHED BY DOW CORNING)

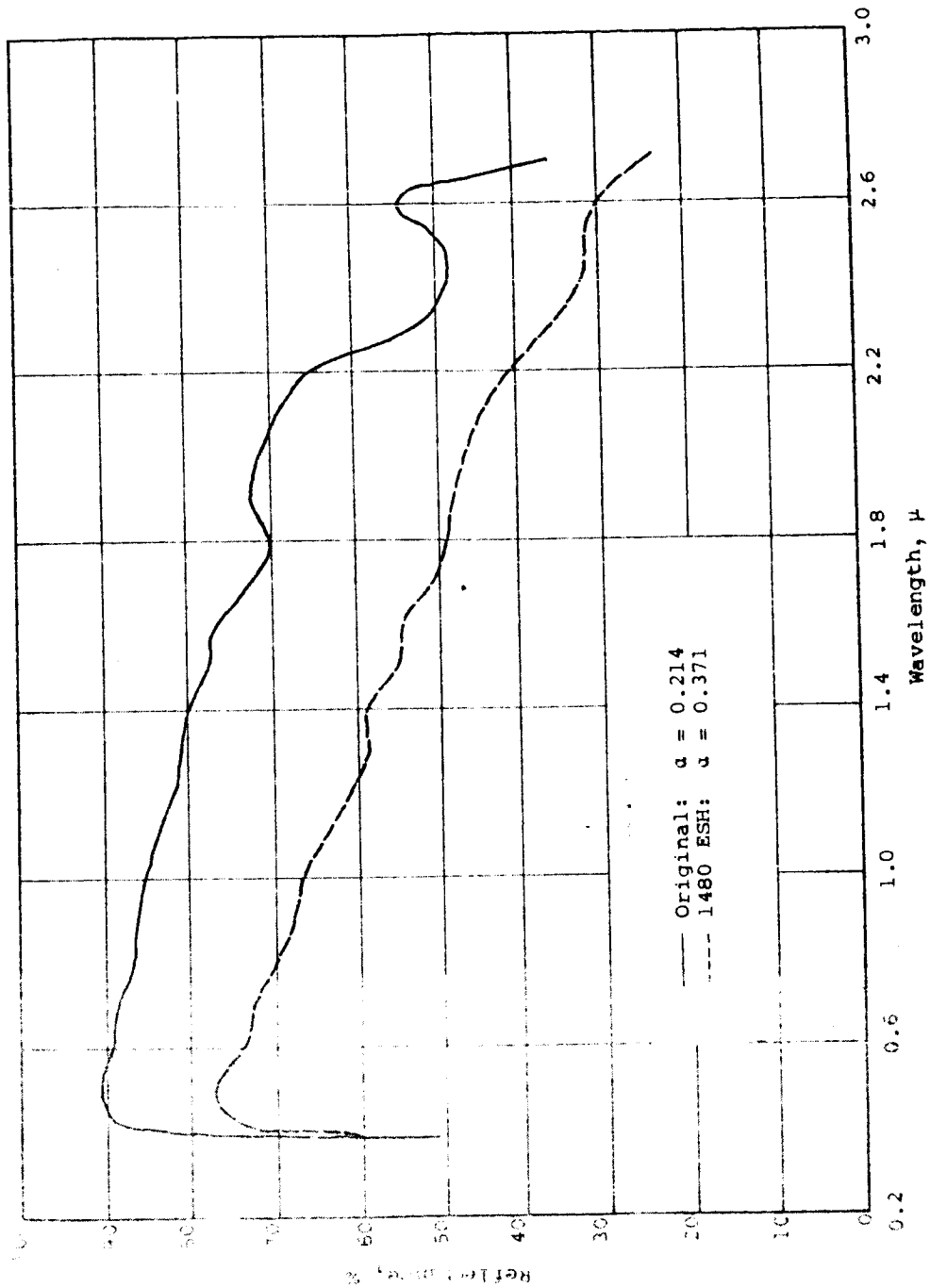


Figure 56
 EFFECT OF 1480 M μ VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT (FURNISHED BY DOW CORNING)

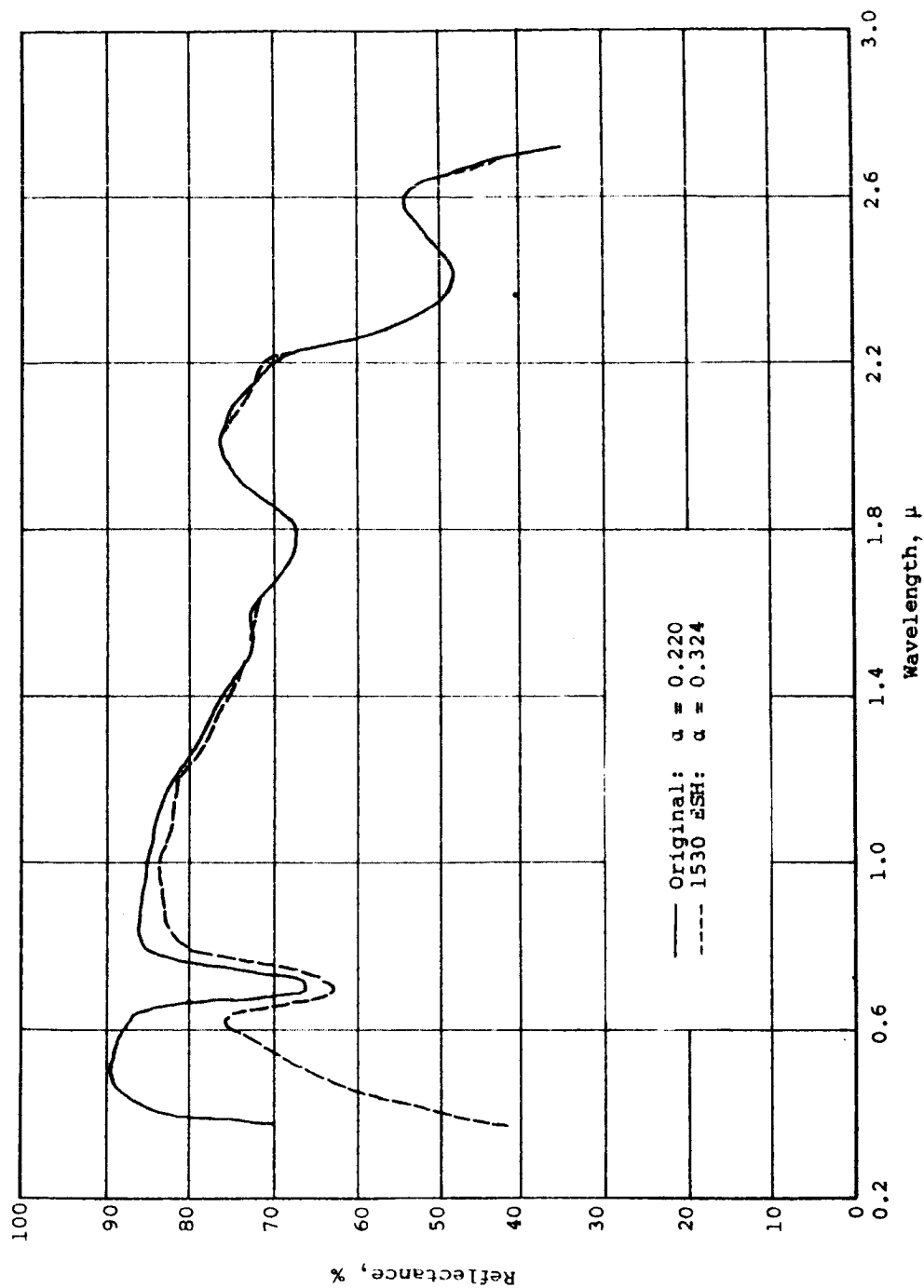


Figure 57

EFFECT OF 1530 ESH IN VACUUM ON SOLAR SPECTRAL REFLECTANCE OF PAINT Q-5-010
(FURNISHED BY DOW CORNING)

Table 31

EFFECT OF 4170 ESH OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF SILICONE PAINTS

| Paint No. | Binder | Composition | | Exposure | | Solar Absorptance | | | |
|-----------|---------|-------------|----------------------------------|-----------|-----------------|-------------------|--------------|--------------|----------------|
| | | PVC, % | Cure | ESH | Solar Factor | α_1 | α_2 | α | $\Delta\alpha$ |
| S-13 | LTV-602 | 30 | 16 hr at room temp. | 0 4170 | 10.6 | .124 .160 | .087 .109 | .211 .269 | .058 |
| S-31 | R-8 | 40 | 1 hr at 300°F | 0 4170 | 10.6 | .145 .165 | .137 .151 | .282 .316 | .034 |
| S-33 | R-9 | 40 | 1 hr at 300°F | 0 4170 | 10.6 | .119 .128 | .097 .108 | .216 .236 | .020 |
| | | | 1 hr at 300°F + 1 hr at 500°F | 0 4170 | 10.6 | .128 .134 | .109 .114 | .237 .248 | .011 |

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Paint S-13 increased 0.058 (18%) in solar absorptance. Coating S-31 increased 12% in solar absorptance, from 0.282 to 0.316, due to degradation. This specimen was applied in a thinner coat than usual, which probably accounts for the unusually high initial solar absorptance.

Paint S-33 was formulated from experimental resin R-9, which was synthesized just prior to Test 23. The 4170-ESH exposure is the only test to which coating S-33 was subjected. The principal difference between R-9 and the other upgraded resins was the pressure at which it was distilled: 0.004 mm Hg for R-9 and 0.04 mm Hg for the other resins. S-33 increased only 9% in solar absorptance.

The S-33 specimen which was heated to 500°F for 1 hour showed the greatest stability to ultraviolet irradiation in vacuum of all the organic and semiorganic paints studied. The increase in solar absorptance of only 0.011, or 4.6%, compares favorably with the best zinc oxide-pigmented potassium silicate paint, which increased 0.008 in solar absorptance in the same 4170-ESH exposure.

IX. DISCUSSION OF SPACE-SIMULATION EFFECTS

A. Testing Procedures

1. Radiation Intensity

The time-intensity reciprocity of the thermal-control coatings of interest was studied. The effect of ultraviolet intensity on the degradation of four potassium silicate paints pigmented with zinc oxide is presented in Table 32. Corresponding samples were: Z69 and Z70, Z71 and Z72, Z73 and Z74, and Z75 and Z76. The uncalcined SP 500 pairs were each formulated and prepared from the same batch at the same time. One-inch-square samples of the calcined pairs were obtained by cutting a 1- x 3-inch painted panel. A significant increase in degradation was apparent at the higher solar factor, indicating that 17 suns was an unrealistically harsh treatment. These results are inconsistent with those for samples Z62, Z64, and Z65 listed in Table 13; stability was good upon irradiation with 17.6 suns.

The effect of ultraviolet intensity on the degradation of four methyl silicone coatings pigmented with zinc oxide and prepared and cured alike is tabulated in Table 33.

Coating S-22 increased 36.5% in solar absorptance during the lower-intensity test; however, it failed catastrophically during the 17-sun test. S-22 was cured with zinc octoate catalyst. The severe degradation which occurred in the 3180- and 3350-ESH tests were therefore not surprising in light of the degradation observed in earlier tests (Table 29).

The solar absorptance of S-18 increased 69% during the 10.7-sun test and 93% during the 17.4-sun test. Similarly, S-13 increased 32% in solar absorptance at 10.7 suns and 51% at 17.4 suns. S-19 again exhibited exceptional resistance to degradation; its solar absorptance increased only 6% in the lower-intensity test. However, like the other paints irradiated in these tests, an increased effect occurred at the higher-intensity exposure: S-19 increased 12% in solar absorptance at 17.4 suns.

The data in Tables 32 and 33 indicate that time-intensity reciprocity is not valid between solar factors of 10.7 and 17.4 intensities for the coatings examined. The question of the validity of photochemical reciprocity, however, was not answered, because the observed increase in degradation may be due in whole or in part to thermal effects or to a discrepancy in the measurement of the solar factors at the two intensities. The choice of 10 suns as the factor for later experiments may not be valid either, since no experiments were conducted at 1 solar intensity. Nevertheless, accelerated tests are imperative for obtaining data in a reasonable amount of time.

Table 32

COMBINED EFFECTS OF VARYING THE SOLAR FACTOR AND OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF INORGANIC ZINC OXIDE COATINGS
All samples cured by air drying.

| Sample | Test No. | Composition * | | | Exposure | | Solar Absorbance | | |
|--------|----------|---------------|---------------------|-------------------|----------|--------------|------------------|------------|----------------|
| | | Pigment | Pigment Calcination | Solids Content, % | ESH | Solar Factor | α_1 | α_2 | $\Delta\alpha$ |
| Z69 | 13 | SP 500 | | 46.3 | 0 | 10.7 | .090 | .067 | .156 |
| | | | | | 3180 | | .119 | .069 | .188 |
| Z70 | 14 | SP 500 | | 46.3 | 0 | 17.4 | .093 | .063 | .156 |
| | | | | | 3300 | | .129 | .074 | .202 |
| Z71 | 13 | SP 500 | | 46.3 | 0 | 10.7 | .095 | .064 | .160 |
| | | | | | 3180 | | .124 | .069 | .193 |
| Z72 | 14 | SP 500 | | 46.3 | 0 | 17.4 | .098 | .068 | .165 |
| | | | | | 3300 | | .130 | .072 | .202 |
| Z73 | 13 | SP 500 | 16 hr at 700°C | 56.9 | 0 | 10.7 | .105 | .067 | .172 |
| | | | | | 3180 | | .136 | .064 | .200 |
| Z74 | 14 | SP 500 | 16 hr at 700°C | 56.9 | 0 | 17.4 | .104 | .067 | .171 |
| | | | | | 3300 | | .157 | .074 | .231 |
| Z75 | 13 | AZO-55LO | 16 hr at 700°C | 56.9 | 0 | 10.7 | .113 | .067 | .180 |
| | | | | | 3180 | | .136 | .072 | .209 |
| Z76 | 14 | AZO-55LO | 16 hr at 700°C | 56.9 | 0 | 17.4 | .115 | .070 | .185 |
| | | | | | 3300 | | .154 | .074 | .228 |

* The binder was PS7 and the PBR 4.30 for all samples.

Table 33

COMBINED EFFECTS OF VARYING THE SOLAR FACTOR AND OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF METHYL SILICONE ZINC OXIDE PAINTS

| Paint No. | Composition [*] | | Exposure | | Solar Absorbance | | | |
|--------------|--------------------------|-----------|--------------|-----------------|---------------------------------|--------------|--------------|----------------|
| | Binder | PVC, % | ESH | Solar Factor | α_1 | α_2 | α | $\Delta\alpha$ |
| S-22 | R-5A | 35 | 0 3180 | 10.7 | .127 .192 | .103 .122 | .230 .314 | .084 |
| S-22 | R-5A | 35 | 0 3300 | 17.4 | Checked, cracked, and fell off. | | | |
| S-18 | SR-80 | 25 | 0 3180 | 10.7 | .130 .243 | .123 .185 | .253 .428 | .175 |
| S-18 | SR-80 | 25 | 33 0 3300 | 17.4 | .125 .284 | .119 .187 | .244 .471 | .227 |
| S-13 | LTV-602 | 30 | 0 3180 | 10.7 | .113 .153 | .086 .110 | .199 .263 | .064 |
| S-13 | LTV-602 | 30 | 0 3300 | 17.4 | .107 .164 | .073 .108 | .190 .272 | .092 |
| S-19 | R-5 | 35 | 0 3180 | 10.7 | .123 .131 | .103 .108 | .226 .239 | .013 |
| S-19 | R-5 | 35 | 0 3300 | 17.4 | .123 .144 | .102 .109 | .225 .253 | .028 |

* S-13 was air-cured, all others were cured 1 hr at 300°F.

2. Exposure Time

Solar absorptance changes of three paints are plotted against the logarithm of exposure (in ESH) in Figure 58. The linear relationship between the absorptance change and the logarithm of exposure obeys the classical Hurter-Driffield equation for photographic materials.¹³

$$A = \gamma (\log E - \log i)$$

where A is the optical density; γ is the slope (the "contrast" in photography); E is the exposure, or product of intensity and time (in joules); and i is the inertia (in joules). Hirt, Schmitt, and Dutton¹⁴ and Schmitt and Hirt¹⁵ have discussed this relation for unpigmented and ultraviolet-absorber-containing films and Zerlaut¹¹ for pigmented films.

The slope and the inertia (the exposure intercept) are a measure of the stability of a system. Exceptionally stable systems possess small slopes and large inertias. While the theoretical basis for the validity of the Hurter-Driffield relation is not well understood even for photographic materials, the relation is probably valid in part at least due to the facts that (1) the films act as filters for ultraviolet, with specific extinction coefficients, and (2) photolyzed materials generally absorb ultraviolet more strongly, with the result that the short-wavelength absorption edge shifts to longer and longer wavelengths. For example, Hirt et al.¹⁴ photolyzed a polyester resin and examined the penetration of yellowing. They analyzed a section of the photolyzed film with a densitometer and found that the optical density at 4358-A wavelength varied inversely with the logarithm of the distance from the exposed surface, as would be predicted from Beer's law.

The usefulness of the Hurter-Driffield relation is that it may permit extrapolation of the curves in order to determine the most extensive damage at long exposures. More work needs to be done on such extrapolation of data. As shown in Figure 58, the long-term behavior of the less stable LTV-602-based paint, S-13, is more easily predicted by extrapolation than the behavior of more stable paints -- especially S-19, which is one of the

¹³Mees, C. E. K., "The Theory of the Photographic Process," MacMillan, New York, 1946.

¹⁴Hirt, R. C., Schmitt, R. G., and Dutton, W. C., Journal of Solar Energy, Vol. 3, No. 2, p. 19, 1959.

¹⁵Schmitt, R. G. and Hirt, R. C., Report WADD-TR-60-704, Feb. 1961.

most stable coatings studied. The scatter in the data for S-19 precluded the drawing of a line through the points. As discussed earlier, the effects of contamination are more readily apparent in stable systems and are obscured in degradable systems, where their effects are less important.

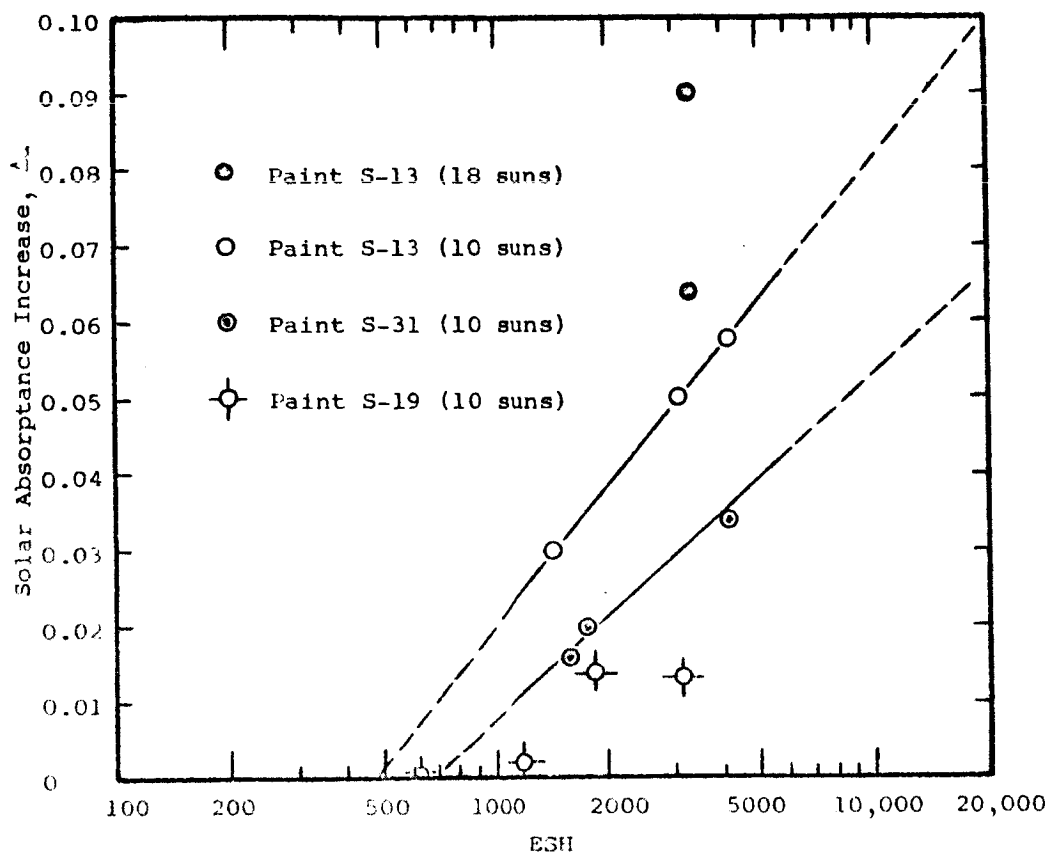


Figure 58

EFFECT OF UV IRRADIATION IN VACUUM
ON SOLAR ABSORPTANCE OF SEVERAL SILICONE PAINTS

3. Vacuum Level

The mechanisms associated with photolysis of methyl silicone polymers and alkali silicates are not understood. Photodecomposition of a molecule in a vacuum is, in general, unlike photodecomposition of the molecule in the presence of oxygen. Oxygen is a diradical in the ground state and hence is a highly efficient scavenger of free radicals. Because the

reaction with oxygen is irreversible, the possibility of chain scission is much greater. In polycarbons, photooxidative degradation is a chain reaction and therefore has a higher quantum yield than would be expected in the absence of oxygen.

Although the vacuum in space is variously reported at 10^{-9} to 10^{-15} mm Hg, we do not believe that the effect of higher vacuum is significant in the study of degradation of nonmetallic materials. The vapor pressure of typical polymers of molecular weight of 100,000 has been calculated as perhaps 10^{-40} mm Hg, so the principal effect of vacuum upon such materials is simply the absence of oxygen. The oxygen pressure at which a particular polymer first undergoes photooxidation as well as photodecomposition probably varies with the nature of the material. An order-of-magnitude calculation for a polycarbon suggests that little oxidation will occur at 10^{-6} mm Hg and at the radiation intensities used in this work.

Assume a solar intensity of 13 milliwatts/cm² in the wavelength range between 2000 and 4000 Å. Assume 75% of this energy is absorbed and that all of the absorbed radiation is effective in breaking bonds. Since about 60 kcal/mole is required to break C-C bonds (and form 2 moles of C radicals), we can calculate the upper limit of radicals formed as:

$$10 \text{ milliwatts/cm}^2 = 2.5 \times 10^{-3} \text{ cal/cm}^2 \text{ sec}$$

$$\frac{6 \times 10^4}{1.2 \times 10^{24}} = \frac{2.5 \times 10^{-3}}{X}$$

$$X = 5 \times 10^{16} \text{ radicals/cm}^2 \text{ sec}$$

In order to produce a similar number of collisions of O₂ with such a surface, the O₂ pressure would be approximately 2×10^{-4} mm Hg, according to the following calculation.

$$\text{The number of collisions/cm}^2 \text{ sec} = \frac{n u}{\sqrt{6} \pi}$$

where n = number of molecules/ml, and u = root-mean-square velocity = $\sqrt{3 R T/M}$. Therefore,

$$5 \times 10^{16} = 0.230 n \sqrt{\frac{(3) (8.3 \times 10^7) (300)}{32}}$$

$$n = 4 \times 10^{12} \text{ molecules/ml}$$

which corresponds to an O₂ pressure of

$$P = \frac{(4 \times 10^{15}) (0.092) (300)}{6 \times 10^{23}}$$

$$P = 2 \times 10^{-7} \text{ atm } O_2 = 2 \times 10^{-4} \text{ mm Hg, pressure of } O_2$$

At these radiation levels, the reaction with O_2 might be appreciable at total pressures above 10^{-3} mm Hg. At higher intensities, the O_2 requirements will be proportionally greater. In our equipment the intensity is from five to ten times greater and the pressure about three orders of magnitude less, so the probability of oxygen scission is negligible.

4. Bleaching

Table 34 presents the results of 450 ESH on three paints. Reflectance was measured immediately after the coatings were removed from the space-simulation chamber and again after they had been stored for about 30 days at ambient laboratory conditions. The data show that the reflectances of S-7 and S-8 returned to approximately their original values before irradiation. Paint S-10 changed little in reflectance, possibly because a temperature of 450°F for 1 hour was required to cure the paint. S-10 was formulated from resin R-4, which has an Me/Si of 1.46. R-4 was synthesized from a mixture of methyltriethoxysilane and dimethyldiethoxysilane. Some surface thermal degradation probably took place on curing, resulting in a decrease in Me/Si and, to conjecture, a matrix which was more transparent (resistant) to ultraviolet resulted.

Table 34

CHANGES IN REFLECTANCE OF SILICONE PAINTS AFTER EXPOSURE
TO 450 ESH AND AFTER STORAGE AT AMBIENT CONDITIONS

| Paint No. | Treatment | Reflectance, % | |
|-----------|----------------|----------------|--------|
| | | 440 mμ | 600 mμ |
| S-7 | None | 87.5 | 92.6 |
| | 450 ESH | 92.5 | 90.5 |
| | 30 days in lab | 86.5 | 92.0 |
| S-8 | None | 80.5 | 92.0 |
| | 450 ESH | 76.0 | 91.5 |
| | 30 days in lab | 84.0 | 92.0 |
| S-10 | None | 77.0 | 87.5 |
| | 450 ESH | 77.0 | 87.0 |
| | 30 days in lab | 79.0 | 87.5 |

The recovery, or bleaching reaction, of discolored paints is demonstrated in Table 34. An explanation of this bleaching phenomenon may be that a large portion of the yellowing of the surface is due to trapped free radicals that are subsequently destroyed by interaction with oxygen in a manner which is analogous to photolysis in the presence of oxygen. The bleaching is rate-controlled by the diffusion of oxygen into the material. Experience has shown that the bleaching is inhibited by refrigeration and exclusion of light, particularly sunlight and light from fluorescent lamps.

The bleaching reaction was a problem only in the evaluation of degradable systems, particularly when solar absorptance increases were 0.10 or greater. Bleaching of zinc oxide-pigmented methyl silicone and potassium silicate coatings was not observed during the first hour or more after removal from the vacuum chamber. Therefore the exposed samples were kept in the dark until their reflectances were measured. The visible reflectance was measured first, because bleaching occurs in the vicinity of 440 mμ. The visible reflectance of the specimens was always measured within an hour after removal from the simulation chamber.

The AH-6 lamp in the ion-pumped chamber was often turned off and the samples visually examined through the quartz window at the completion of a simulation test, while the vacuum was still in the range of 10^{-7} torr. Without exception, the zinc oxide-pigmented methyl silicone and potassium silicate paints were white and undamaged, but the adjacent degradable systems -- rutile- and zinc sulfide-pigmented methyl-phenyl silicones, rutile-pigmented methyl silicones, rutile-pigmented epoxies, and perhaps most significantly, zinc oxide-pigmented methyl-phenyl silicones -- were yellow and severely discolored.

B. Photolysis Mechanisms

1. Pigment

Much has been learned about zinc oxide and other oxides through studies of catalysis and photoconductivity, but rates of separation of photolyzed metal and oxygen are not known. It is conceivable that solar radiation might produce negligible photolysis, even in the high vacuum of space.

To prevent undesired photolysis, the problem is essentially the opposite of trying to make a good photoconductor or semiconductor. Light produces an excited state or nonequilibrium condition which persists for a relatively long time in a photoconductor. During this time atoms in the lattice may diffuse to more stable sites. For example, silver in silver bromide diffuses toward segregated silver metal particles, which grow

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as photolysis proceeds. If the diffusion of the silver were more restricted, the photolysis would be less efficient. A zinc oxide of high solar stability should therefore be a poor photoconductor, and the diffusion rate of excess zinc (actually interstitial Zn^{+}) should be low

In the following discussion zinc oxide is used as the prime example because it has been studied more than any other metal oxide, but the principles involved apply to magnesium oxide, zirconium dioxide, titanium dioxide, and other oxides suitable for pigments. A consistent picture of zinc oxide behavior has been worked out only in the past few years.

Collins and Thomas¹⁶ have analyzed the behavior of zinc oxide. It is normally an n-type conductor. When its surface absorbs oxygen, a negative surface layer composed of oxygen ions forms and an electron depletion layer or space charge develops below the surface. Diffusion of photolysis products proceeds in this depleted layer. On the other hand, when the surface is reduced with hydrogen or absorbs zinc atoms, a conductive "enrichment" layer with a high concentration of donors forms near the surface. An enrichment layer having the same characteristics can be produced by photolysis. The light produces hole-electron pairs which break up and diffuse in the surface field. The holes discharge surface oxygen ions and generate oxygen molecules which then evaporate. Further photolysis releases oxygen from the lattice and leaves excess zinc. This zinc remains dissolved in the lattice, at least in the early stages of photolysis, as interstitial Zn^{+} ions. These ions are not stable in the presence of oxygen, and they are concentrated in the centers of the crystals. The high free-electron concentrations that are generated by light tend to discharge Zn^{+} ions and precipitate zinc metal, but other factors may hinder this reaction. The rate of diffusion of the Zn^{+} is particularly important.

Past work on the photolysis of silver bromide is helpful in analyzing possible mechanisms in pigments. Large single crystals of oxides show less photolysis than powders subjected to the same exposure. In silver halides the silver ions near imperfections or surfaces are more vulnerable to reduction by free electrons generated by light than silver ions at normal lattice sites. These surface or imperfection effects could be important in the photolysis mechanisms of oxides. At one surface, free oxygen may be generated; at another surface less exposed to the light or more favorable for metal separation, the free metal may separate. In other words, light generates

¹⁶Collins, R. J. and Thomas, D. G., Physical Review, Vol. 112, p. 338, 1958.

electric field and concentration gradients which are equalized by the separation of the elements in the oxide. In fact, an analogous argument can be advanced for the reason why quartz windows are virtually unaffected by ultraviolet irradiation in vacuum but powdered quartz (silica) is severely degraded. A similar argument can be advanced for magnesium oxide windows versus magnesium oxide powder.

In silver bromide the photolysis is sensitized by small islands of silver sulfide, gold, or silver itself. These islands trap electrons, which later reduce silver ions. Trapping is important because it increases the lifetime of chemically active excess carriers. When zinc oxide is made so that small islands of zinc metal remain in the oxide crystals, these crystals might be unusually sensitive to photolysis. This sensitivity could mean that once photolysis produces metal, further photolysis of the satellite coating might be rapid and catastrophic.

We studied methods of detecting small traces of excess metal in oxides or other systems for the specific purpose of evaluating pigments and photolysis mechanisms. The two methods we found to be most applicable are described in Section X on related investigations.

In pigment-vehicle systems the vehicle can be oxidized by the oxygen that is generated by photolysis. Peroxide ions may be involved, but the mechanism is the same. In silver bromide-gelatin emulsions bromine attacks the gelatin or is removed by developing chemicals. If the anionic element could be kept from reacting with the vehicle or from diffusing out of the paint, increased stability would result. Experimental data on the diffusion of oxygen through organic membranes, which are similar to the vehicles used in paints, show wide variation. In space, such diffusion could be a limiting factor in photolysis of a coating. If the oxygen in zinc oxide paints did not escape but reacted instead with Zn^+ ions or free zinc that was produced in the lower or back parts of the coatings, the net result would be a conversion of light into heat.

When zinc oxide crystals are exposed to zinc vapor at elevated temperatures and cooled rapidly to room temperature, they acquire a red or yellow color due to "dissolved" excess zinc. From conductivity data, Thomas¹⁷ determined the concentration of excess zinc in equilibrium with zinc metal at temperatures of 450 to 700°C. Data from his plot of solubility (in atoms of excess zinc per cubic centimeter of the crystal) are recorded in Table 35.

¹⁷Thomas, D. G., The Journal of Physics and Chemistry of Solids, Vol. 3, p. 229, 1957.

Table 35

SOLUBILITY OF ZINC IN ZINC OXIDE FROM SATURATED VAPOR

| Temperature, °C | Concentration of Zinc Atoms |
|--------------------|-----------------------------------|
| 800 | 3×10^{17} |
| 600 | 6×10^{16} |
| 500 | 2×10^{16} |
| 400 | 5×10^{15} |
| 300 | 8×10^{14} |
| 162 | 10^{13} |
| 72 | 10^{11} |

Photolysis by light in a vacuum can produce the same excess zinc concentrations. When crystals which have been exposed to zinc vapor are quenched, why does the zinc not segregate? The diffusion coefficient for interstitial excess zinc in the temperature range from 180 to 350°C is given by Thomas as:

$$D = 2.7 \times 10^{-4} \exp (-0.55/k T)$$

where $k T$ is in electron volts.

At 300°K, $D = 7.3 \times 10^{-14}$. For a sphere of radius 10^{-5} cm around a zinc metal particle, the concentration gradient might be about 10^{22} atoms of interstitial zinc per cubic centimeter per centimeter in photolyzed material. Such a gradient could exist over a distance of 10^{-5} cm between yellow zinc oxide and the surface of a segregated zinc particle. This condition corresponds to a transfer rate of about 0.02 atom of excess zinc per second to the zinc particle. A zinc particle of 100-A radius would require about 1.2×10^6 seconds, or 140 days, to build up these conditions. In other words, if nucleation started, darkening due to metal separation could develop over a period of months at 300°K. This slow diffusion rate of interstitial zinc may be responsible for the apparent stability of quenched zinc oxide crystals that contain excess zinc. However, the possibility of diffusion of oxygen should be considered also.

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Particularly significant is the effect of interstitial zinc produced by photolysis on the lifetime of excess carriers generated by light. Although a hole has the same positive charge as interstitial Zn^+ , high polarization effects around an interstitial Zn^+ may favor hole capture and recombination. If this is the case, the stability of zinc oxide in light may stem from this increased recombination after a certain concentration of interstitial Zn^+ is produced by the light. In magnesium oxide, aluminum oxide, and zirconium oxide, which are more easily photolyzed by light, interstitial cations are not readily formed, either because of the compact lattices or because of the large size of the Zr^+ cation. This means that magnesium, aluminum, and zirconium are not as soluble in their oxides as zinc is in zinc oxide. Since there are ways of reducing excess carrier lifetime by adding impurities different from the host cation, the addition of impurities is of interest. Such methods have been tried, but much work remains to be done on correlation with the types and quantities of impurities added.

2. Binder

Since the predominant photochemical reactions in a high vacuum are cross-linking and color center formation, large changes in the physical properties of plastic structural members will not occur in a vacuum, particularly in the absence of any accompanying thermal effects. Thus, for polymeric materials which do not undergo catastrophic main-chain cleavage, the predominant physical changes will be discoloration and surface embrittlement as a result of cross-linking. The cross-linking can be considered as self-limiting, since the polymer material acts as a filter which possesses a high extinction coefficient for ultraviolet, particularly for the more damaging, shorter wavelengths.

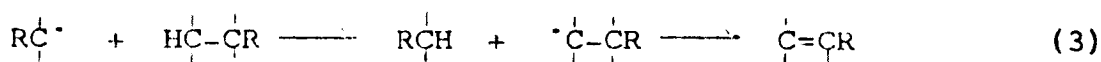
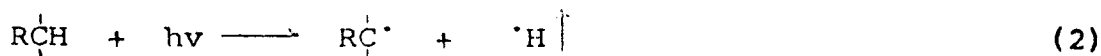
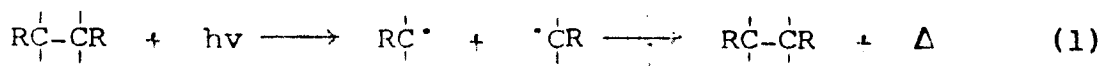
Thus, the primary concern in the utilization of pigmented organic, semiorganic, and inorganic coatings for the purposes of spacecraft thermal control is the prevention of color center formation (i.e., coloration which increases the solar absorptance). The secondary concern is the prevention of erosion of the surface due to main-chain cleavage, side-chain cleavage, or both.

The aim of photochemical investigation is to determine the mechanisms associated with the chemical change which occurs when a substance absorbs ultraviolet light. The reactions are complex, and the actual change measured is seldom that produced by the primary process of light absorption. Therefore it is necessary to distinguish between the "primary" effect of ultraviolet and the "secondary" thermal reactions which follow. The frequent production of atoms or radicals in photochemical processes leads to extremely complex secondary reactions.

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The basic difficulty in studying the formation of radicals in solids was pointed out by Franck and Rabinowitch,¹⁸ who discussed the cage effect. This effect, often described as the Rabinowitch cage effect, is associated with the framing of a free radical by its surrounding molecules in such a way that free-radical recombination prevails. Such an effect may account for the fact that the gamma irradiation of higher hydrocarbons at 77°K results in the cleavage of C-H rather than the weaker C-C bonds.^{19,20} That is, the cage effect may permit the diffusion of hydrogen and simultaneous trapping of the larger carbon radicals, which subsequently recombine.

The predominant reaction in the photoinduced decomposition of polymers in the presence of oxygen is oxidative, unless the polymer unzips to yield monomer. The quantum yields in the absence of oxygen are much lower than in its presence, due to the cage effect. When C-C bonds are part of the polymer backbone, they cannot diffuse away rapidly enough and, as a general rule, recombination and cross-linking occur. By contrast, when a C-H bond is broken, the hydrogen atom formed is highly mobile and the statistical probability of recombination is reduced. Thus, the eventual reaction is the production of a molecule of hydrogen and the formation of a new cross-link, representing the combination of two volatile (hydrogen) fragments and two residual, nonvolatile fragments, respectively. This does not preclude the existence of various chain transfer steps as intermediate reactions, but these do not contribute to the net reaction.



Thus, the creation of stable molecular species is encouraged by: (a) back reaction, (b) cross reaction, and

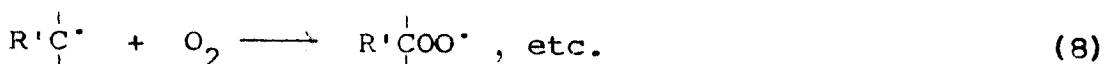
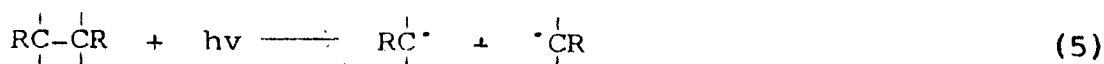
¹⁸ Franck, J. and Rabinowitch, E., Transactions of the Faraday Society, Vol. 30, p. 120, 1934.

¹⁹ Norman, I. and Porter, G., Nature, London, Vol. 174, p. 508, 1954.

²⁰ Smaller, B. and Matheson, M. S., The Journal of Chemistry and Physics, Vol. 28, p. 1169, 1958.

(c) molecular rearrangement. Should the higher-molecular-weight radical (RC^\bullet or $^\bullet\text{C}-\text{CR}$ in Equations 2 and 3 be sufficiently immobilized, or trapped, the possibility of providing a permanent color center in the absence of oxygen or a similar reactive substance is apparent. Lawton et al²¹ claim that radical trapping in polymer systems occurs under three conditions: (a) within the crystallites of the polymer, (b) in the amorphous phase below the glass transition temperature, and (c) in heavily cross-linked polymers, because they may be attached to a network structure in a position in which no other radical is accessible.

In the presence of oxygen, the possibility of chain scission is much greater, due to the irreversibility of the reaction with oxygen. Moreover, this is a chain reaction and can therefore be expected to have a higher quantum yield.



Miller²² has shown by electron spin resonance that irradiated polyvinyl chloride which has been exposed to air loses radicals at a far greater rate than samples treated similarly in a vacuum. Chapiro²³ reports a lack of coloration of the material when it is exposed to air and attributes it to the formation of the peroxy radical. St. Pierre and Dewhurst²⁴ found it possible to totally inhibit the formation of C-C cross-links by the introduction of sufficient oxygen. These same authors, in another paper,²⁵ describe the oxygen termination

²¹ Lawton, E. J., Balwit, J. S., and Powell, R. S., *Journal of Polymer Science*, Vol. 32, pp. 257 and 277, 1958.

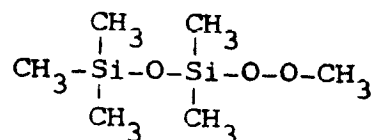
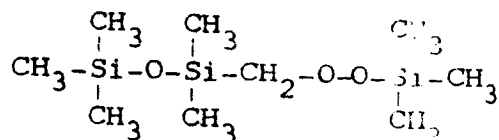
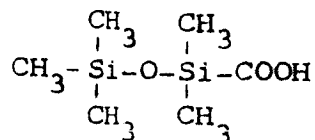
²² Miller, A. A., *Journal of Physical Chemistry*, Vol. 62, p. 1755, 1959.

²³ Chapiro, A., *The Journal of Chemistry and Physics*, Vol. 53, p. 895, 1956.

²⁴ St. Pierre, L. E. and Dewhurst, H. A., *The Journal of Chemical Physics*, Vol. 29, p. 241, 1958.

²⁵ St. Pierre, L. E. and Dewhurst, H. A., *Journ. of Physical Chemistry*, Vol. 64, p. 1060, 1960.

of free radicals in irradiated siloxane. They found a carboxylic acid and two types of peroxides were formed during radiolysis of hexamethyldisiloxane:



The foregoing analysis provides a general picture of the various possible photochemical reactions and their complexity, against which the results of this program can be evaluated. Upon irradiation with ultraviolet in vacuum, the methyl silicones proved to be among the most resistant materials known. This is not surprising, since short alkyl groups (e.g., methyl) are inherently more transparent to extraterrestrial ultraviolet than both longer-chain alkyl and phenyl groups. Finally, the -Si-O-Si-O- backbone possesses a quartzlike structure which is both relatively transparent to ultraviolet and at the same time is thermally resistant.

X. DISCUSSION OF RELATED INVESTIGATIONS

A. Photolysis of Zinc Oxide

A better understanding of the photolysis mechanism in zinc oxide could lead to much improved stability of zinc oxide, titanium dioxide, zirconium dioxide and other high-index pigments. The first step is to be able to quantitatively measure the degree of chemical photolysis. The optical effect of reduced metal "dissolved" in a lattice as defects is distinctly different from the optical effect of segregated metal particles. Oxides that dissolve excess metal and those that do not may have the same degree of photolysis, as measured by chemical analysis, but a large difference in optical properties. Variations in the impurity content of the same oxide can also be expected.

In addition to defining the difference between dissolved and segregated metal, we also are interested in reducing the efficiency of the photolysis itself. If the photon energy can be converted more effectively to thermal vibrations, less chemical and optical degradation will result. The basic idea is to make a poor photoconductor by introducing recombination centers for excess electrons and holes.

Two methods for measuring degree of photolysis were explored. One depends on the reducing action of zinc and other metals on nitrites. The other involves the reaction of the metal with an acid to produce traces of hydrogen, measured in a precision volumetric vacuum system.

1. Method 1

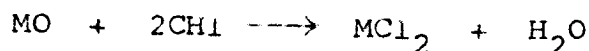
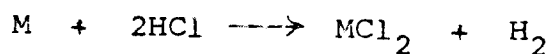
The nitrite reduction method was tested and looks promising for compounds containing excess zinc in the range of parts per thousand. The metals above hydrogen in the electromotive series reduce the nitrite ion when dissolved in dilute acid. Under optimum conditions, which have been established for small quantities of free metal, the reduction is quantitative. If the amount of nitrite ion is stoichiometrically in excess of the metal, it is possible to determine the metal by an indirect spectrophotometric method.

Much work has been done at IITRI on nitrites in azides. The n-(1-naphthyl)-ethylenediamine dihydrochloride and sulfanilic acid reagent is a sensitive colorimetric reagent for nitrogen dioxide or nitrite ions in azides in parts per

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million.^{26,27} The reagent-nitrite ion complex is a stable red-violet color. The intensity of this color is measured at 550 mμ. The fact that traces of nitrite ion can be separated from the azide by using this reagent makes possible some interesting techniques, since nitrite salts and acid in solution immediately react with azides. This reaction is the basis for a quantitative determination of azides.²⁸⁻³⁰

Trace quantities of free metal in a metal oxide are difficult to detect and are below the sensitivity range of x-ray techniques. When an acid such as hydrochloric acid reacts with a metal according to the displacement reaction, hydrogen is released, while the acid reaction with the metal oxide yields water:



Hydrogen in the nascent state is a strong reducing agent and reduces nitrogen and nitrogen compounds to ammonia.

The color intensity of the n-(1-naphthyl)-ethylenediamine dihydrochloride and sulfanilic acid reagent in the presence of the nitrite ion is proportional to the concentration of nitrite ion present. The basis for the analytical procedure is that the amount of metal dissolved in excess acid is directly proportional to the hydrogen released, and the decrease in absorbancy of the reagent-nitrite ion complex is proportional to the hydrogen formed. Therefore it is proportional to the amount of metal dissolved.

Preliminary experiments using known quantities of finely divided zinc metal and zinc oxide indicated the soundness of the analytical procedure. Figure 59 shows the decreasing

²⁶ Saltzman, E., Analytical Chemistry, Vol. 26 p. 1949, 1954.

²⁷ Combs, H. F. and Grove, E. L., Talanta, Vol. 9, p. 453, 1962.

²⁸ Reith, J. F., Dissertation, Utrecht, 1929.

²⁹ Kolthoff, I. M. and Belcher, R., "Volumetric Analysis," Interscience Publishers, Inc., New York Vol. III, p. 661, 1957.

³⁰ Reith, J. F. and Bowman, J. H. A., Pharmaceutisch Weekblad, Vol. 67, p. 97, 1930.

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absorbance with the increase in zinc. The unirradiated SP 500 zinc oxide possessed 2596 ppm of Zn^0 (Matthey Spec pure zinc oxide contained no excess zinc). After 43 hours of irradiation in vacuum (AH-6 lamps at 5-cm distance from specimen), the zinc oxide contained 3795 ppm Zn^0 , or an increase of 1199 ppm excess zinc due to ultraviolet irradiation in vacuum. Some additional work is needed to perfect the techniques and to secure purer reagents.

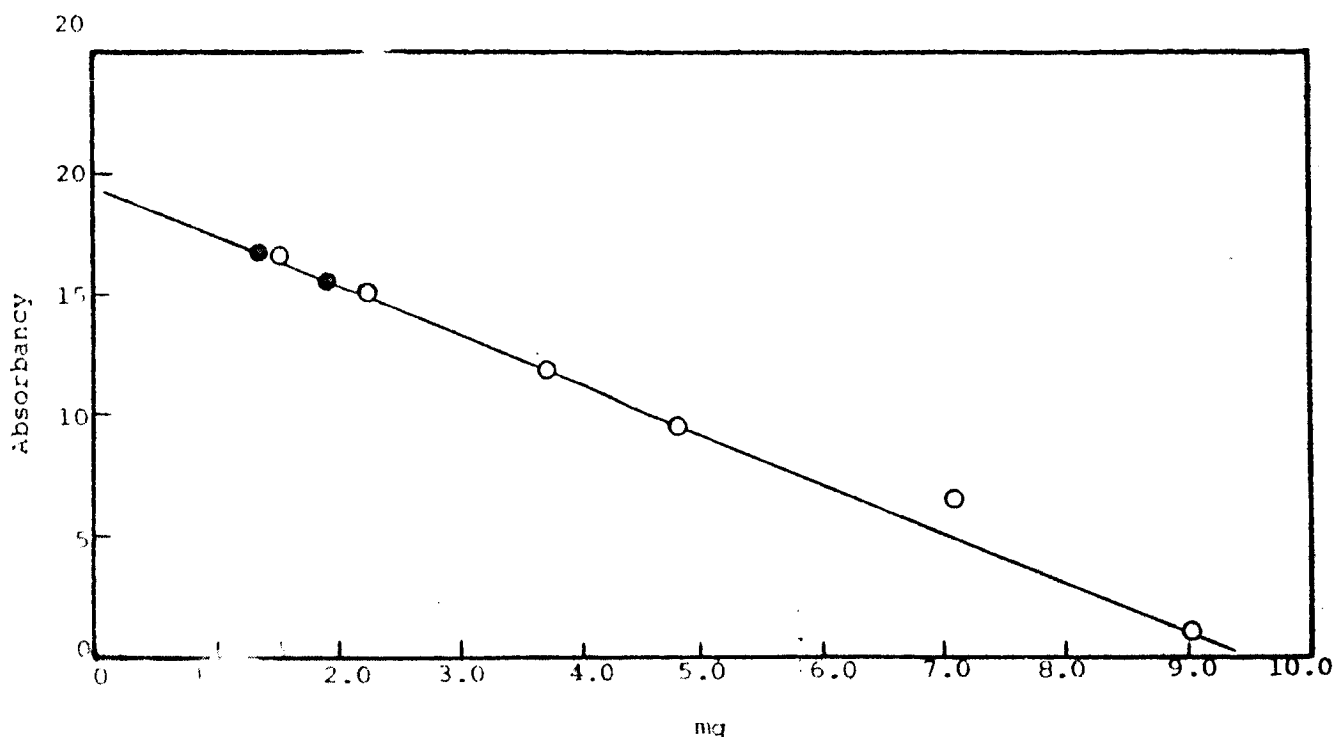


Figure 59

CALIBRATION CURVE FOR SPECTROPHOTOMETRIC DETERMINATION
OF Zn^0 IN ZINC OXIDE

These principles and the proposed procedures should also be usable with $Sn-SnO_2$ and other systems that undergo the displacement reaction with hydrochloric or sulfuric acid. Presently one of the major difficulties is obtaining reagents of the desired purity.

Experimental. A series of standards of pure metallic zinc (200 mesh) ranging from 1.5 to 9.0 mg plus 500.0 \pm 2.9 mg of Matthey Spec pure zinc oxide were placed in 100-ml Nessler tubes. Exactly 20.0 ml of standard NO_2^- solution (0.005 mg N/ml) was added to each. Four ml of 1:1 HCl was then added. Boiled and cooled distilled water was added to each tube to the 100-ml mark. The tubes were then closed with corks covered with Saran Wrap and were inverted several times to mix the contents thoroughly. Checks were set on 500 mg of the ZnO and the HCl alone without any metallic zinc to observe the effect on the standard NO_2^- solution; 500.0 \pm 1.0 mg of the radiated and nonradiated ZnO were treated the same as the standards. The tubes were allowed to stand for 48 hr. Ten-ml aliquots were then withdrawn and transferred to 100-ml volumetric flasks. Finally, the NO_2^- nitrogen remaining in the standards, the checks, and the unknown samples was determined spectrophotometrically by the n-(1-naphthyl)-ethylenediamine dihydrochloride and sulfanilic acid procedure. The results are tabulated in Table 36.

Table 36
DETERMINATION OF EXCESS ZINC IN ZINC OXIDE

| ZnO | Zn ^o | 1:1 HCl, ml | NO_2^- Std., ml | Absorpancy at 500 m μ |
|-------|-----------------|----------------|-----------------------------|------------------------------|
| 500.3 | | 4 | 20 | 0.195 |
| 501.1 | 1.5 | 4 | 20 | .165 |
| 502.3 | 2.2 | 4 | 20 | .150 |
| 501.8 | 3.6 | 4 | 20 | .120 |
| 502.9 | 4.8 | 4 | 20 | .095 |
| 501.5 | 7.1 | 4 | 20 | .065 |
| 501.0 | 9.0 | 4 | 20 | .013 |
| | Control | 2 | 20 | .195 |
| 500.8 | Not irradiated | 4 | 20 | .167 |
| 500.4 | Irradiated | 4 | 20 | 0.155 |

2. Method 2

The procedure used was developed by Allsopp.³¹ The sample is dissolved in hydrochloric acid in a vacuum. By this means solid zinc oxide is completely broken down, giving the excess metal the opportunity to react with the acid and to form an equivalent amount of hydrogen. The acid is evaporated to ensure that all the evolved gas is released. Hydrochloric acid vapors are condensed in liquid nitrogen traps, and dry hydrogen chloride is absorbed by soda asbestos. The pressure of the evolved gas is measured by a Pirani gauge. Any oxygen present is allowed to react with the hydrogen on a platinum filament at 600°C. and the pressure drop is measured. The remaining hydrogen is diffused into the atmosphere through a palladium tube at 350°C. and the pressure drop is again measured. The total hydrogen present is found from the two pressure changes, and the zinc equivalent is then calculated.

³¹ Allsopp Analyst. Vol. 32, p. 474. 1957.

Figure 60 is a diagram of the apparatus, and Figure 61 is a photograph of the system we constructed. The apparatus consists of two parts, a reaction system and an analytical system. The reaction system consists of four bulbs, which can be cooled with liquid nitrogen. Bulb 1 is provided with a side arm which houses the sample and a sealed glass tube, filled with iron powder, which acts as a pusher. Bulb 2 is provided with a side arm through which 50% v/v hydrochloric acid can be added. Both side arms are sealed with a torch after the sample pusher and the acid are in the system. The reaction vessels are connected to the main apparatus by a cone-and-socket joint, then to a mercury-vapor cold trap (1) and tap (T_1), and then to a three-stage mercury diffusion pump (P_1). This pump transfers the evolved gases from the reaction vessels to an analytical system containing a palladium tube, a platinum filament, a Pirani gauge, a soda-asbestos bulb, a McLeod gauge, and a cold trap (2). The palladium tube, soda-asbestos bulb, McLeod gauge, and cold trap can be isolated from the analytical system by taps. A second mercury diffusion pump (P_2) is used to evacuate the whole system and is backed by a rotary oil pump. When necessary, the reaction vessels can be directly evacuated by this backing pump via a tap (T_u).

B. Physical Sensitivity of Zinc Oxide

Yellowing of zinc oxide coatings was produced by various treatments: scratching of the surface, grinding with an agate mortar and pestle, and compacting at high pressures. This discoloration was not apparent on the bottom surface of the coating adjacent to the substrate when the coating was removed in one piece.

Pellets of SP 500 and E-P 730 zinc oxide were compacted at pressures of 10,000 and 50,000 psi. The yellowing phenomenon is evident from the total reflectance measurements listed in Table 37. A Photovolt photoelectric reflection meter utilizing a green filter was used for the reflectance determinations. The samples were heated for 16 hours each in various atmospheres: argon with titanium sponge in the system, argon, and oxygen. When heated in the argon-titanium sponge system, a startling color change to a blue-gray occurred in SP 500 and a slight graying occurred in E-P 730.

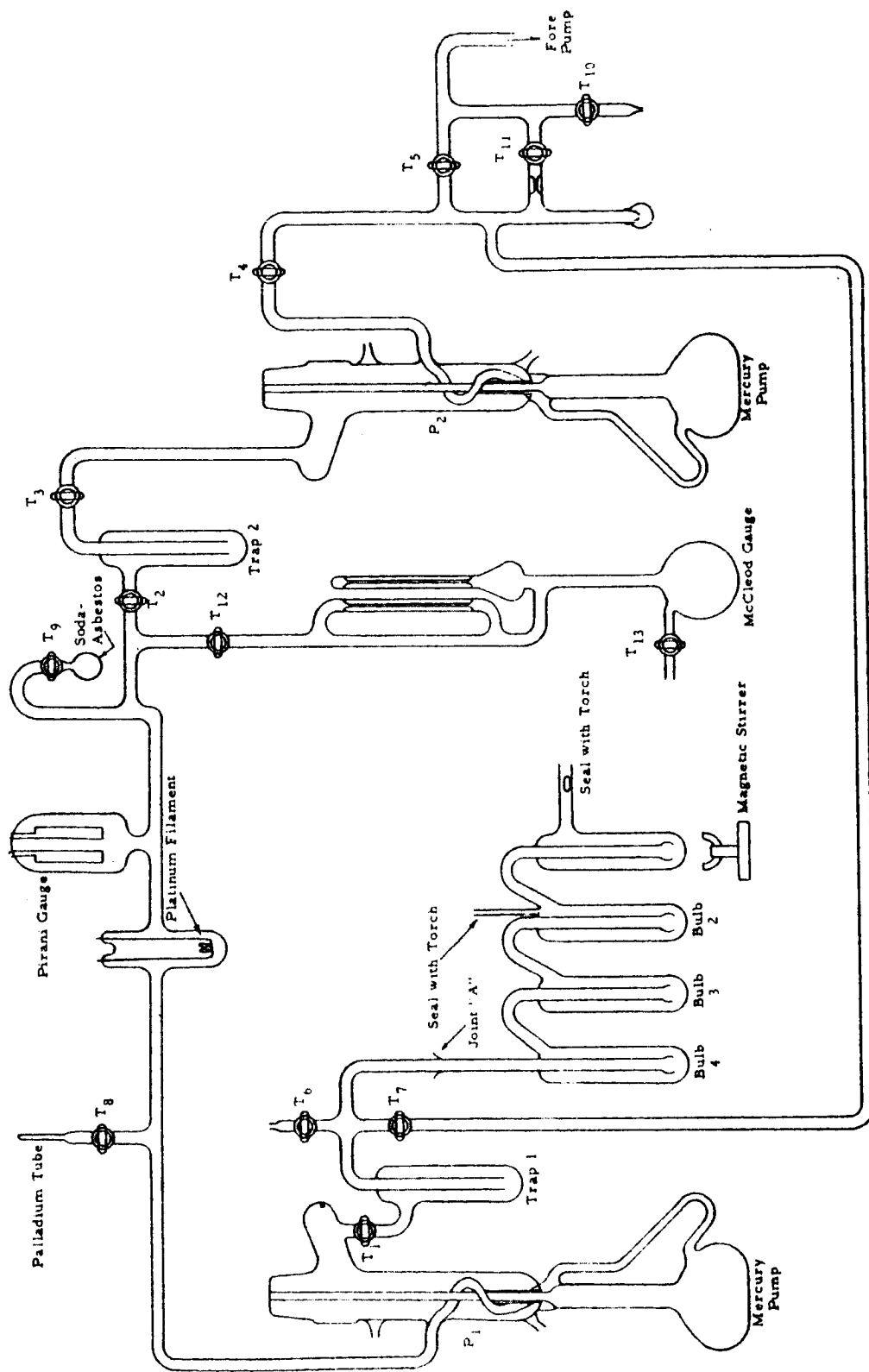


Figure 60
SCHEMATIC OF REACTION AND ANALYTICAL SYSTEM FOR DETERMINATION
OF INTERSTITIAL Zn^{+} AND EXCESS Zn° IN ZINC OXIDE

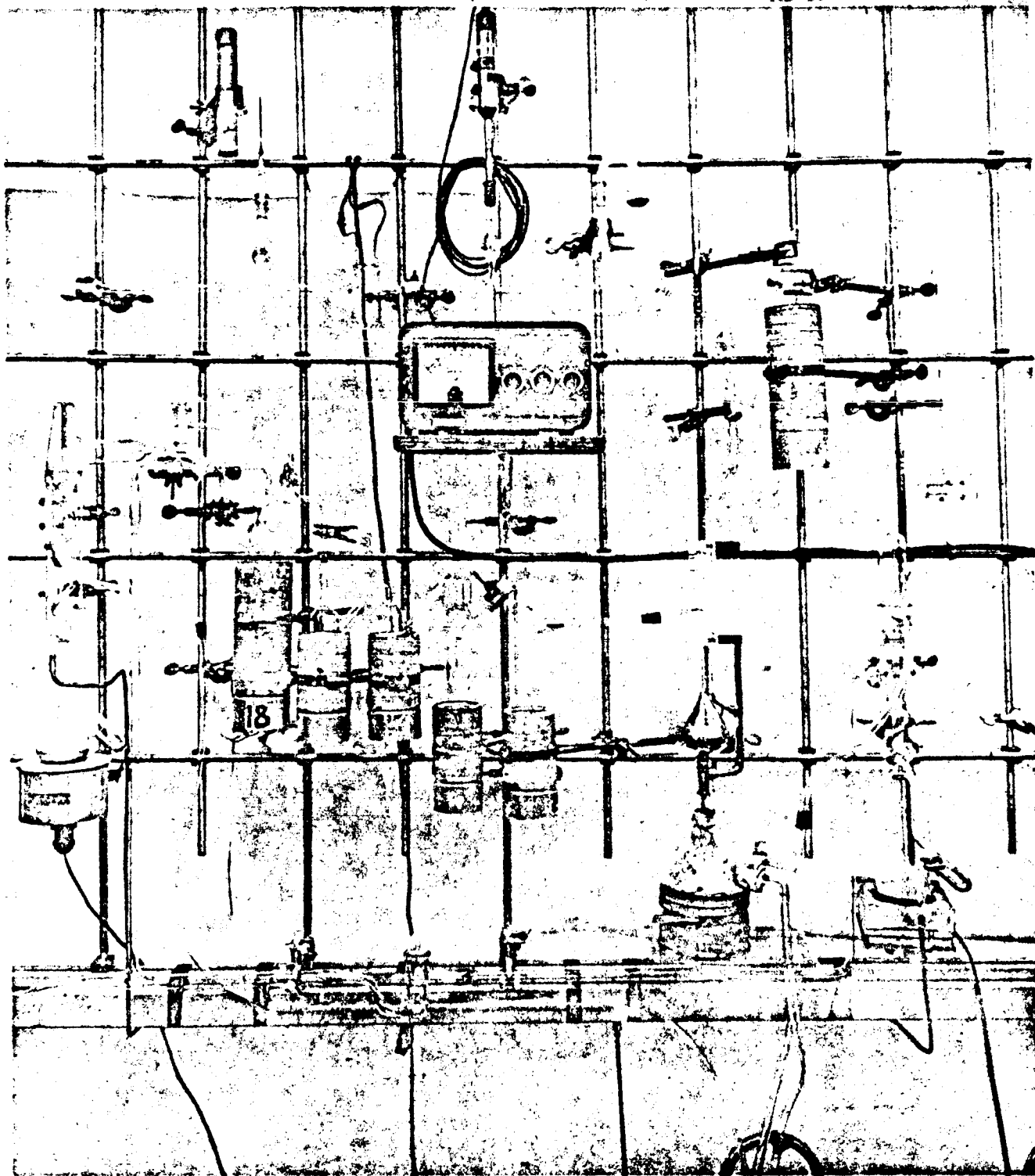


Figure 61

REACTION AND ANALYTICAL SYSTEM FOR DETERMINATION
OF INTERSTITIAL Zn^{+} AND EXCESS Zn° IN ZINC OXIDE

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Table 37

REFLECTANCE OF ZINC OXIDE PELLETS
FIRED AT 500°C IN VARIOUS ATMOSPHERES

| Atmosphere | Reflectance of SP 500, % | | Reflectance of E-P 730, % | |
|-----------------------|--------------------------|------------|---------------------------|------------|
| | 10,000 psi | 50,000 psi | 10,000 psi | 50,000 psi |
| As pressed | 99.5 | 95.5 | 81.5 | 76.5 |
| Argon-titanium sponge | * | 19.0 | * | 74.0 |
| Argon | 68.5 | 59.0 | 78.0 | 68.5 |
| Oxygen | 98.5 | 98.5 | 86.0 | 81.5 |

* These samples were not measured; they were similar in color to their 50,000-psi counterparts.

Examination of the titanium sponge, which was incorporated in the system to remove traces of oxygen in the argon, revealed considerable oxidation. Heating of the discolored ZnO pellets in air at 500°C for 1 hour restored them to their original color. Evidently the use of the sponge as an oxygen getter with argon yielded an atmosphere conducive to reduction of zinc oxide. Removal of titanium from the system did not completely eliminate this reduction, as seen in the value for the argon run in Table 37. Again, SP 500 was more sensitive to oxygen removal than E-P 730. An oxidizing atmosphere partially bleached the SP 500 pigment and to a more marked degree bleached the 730 pigment. Thus, the yellow color appears to be due to interstitial zinc or oxygen ion deficiency.

C. Binder-Rich Layers (Gloss)

A protective effect of increasing PVC on ultraviolet stability was demonstrated. Yellowing of zinc oxide pigments was shown to be inversely dependent on PVC. Since ultraviolet damage occurs only in the outermost layers (approximately 5 μ) of these paints and since some pigment probably settles before the vehicle "sets," an unprotected, pigment-deficient (glossy) layer might contribute to the observed degradation.

Accordingly, an experiment was designed to determine the extent of the contribution to degradation of a pigment-poor layer, if present. For the purposes of defining the problem, a moderately degradable paint was chosen rather than one of the more stable coatings. Four 1- x 3-inch aluminum panels were abraded and coated with paint S-1, a zinc sulfide methyl-phenyl silicone with a PVC of 40%. The coatings were applied at thicknesses in excess of 3 mils, allowed

to air-dry for 24 hours, and then baked at 300°F for 16 hours and at 400°F for 2 hours. Two of the coatings were gently scraped with a razor blade in order to remove the top layers; approximately 0.5 mil was removed.

The results after exposure to a simulated space environment are presented in Table 38. The data indicate that a pigment-deficient glossy layer was originally present and that it contributed significantly to the degradation of the untreated samples. The higher reflectance of the scraped samples than that of the untreated samples before exposure to space simulation is further indication of the existence of a binder-rich layer. While the existence of a binder-rich layer is not as serious in the more stable zinc oxide-pigmented methyl silicones (e.g., LTV-602), it will be significant when such paints are exposed to 4000 or more ESH.

Table 38
EFFECT OF REMOVAL OF GLOSSY LAYER
ON REFLECTANCE OF PAINT S-1

| Glossy Layer | Exposure, ESH | Reflectance, % | | | | |
|--------------|------------------|----------------|--------|--------|--------|--------|
| | | 400 mμ | 440 mμ | 500 mμ | 600 mμ | 700 mμ |
| Present | 0 | 72.0 | 83.9 | 88.0 | 87.6 | 59.0 |
| | 315 | 35.5 | 50.8 | 68.6 | 81.5 | 59.2 |
| Present | 0 | 72.0 | 82.5 | 85.0 | 83.5 | 58.8 |
| | 315 | 39.0 | 53.2 | 68.5 | 78.2 | 58.0 |
| Scraped off | 0 | 75.0 | 86.4 | 89.3 | 88.7 | 60.0 |
| | 315 | 51.2 | 66.2 | 78.6 | 85.4 | 60.0 |
| Scraped off | 0 | 73.0 | 84.1 | 86.3 | 84.7 | 59.5 |
| | 315 | 44.5 | 59.0 | 73.0 | 80.5 | 58.5 |

D. Composite Coatings

Composite inorganic-organic coatings were of interest for combining the advantageous properties of the respective layers, i.e., the space stability of a ceramic paint and the physical properties of a polymeric coating. The organic layer also provides a protective film on aluminum for aluminum phosphate paints.

Wetting of various organic coatings with silicate formulations was aided by lightly preblasting with fine silicon carbide. An alternative method of application for phosphate paints was to smear the organic with a thin coating of the inorganic, followed by drying. This procedure produced a wettable, adherent film.

Other methods were attempted to obtain improved wetting. Incorporation in ceramic paints of water-soluble organic surface tension depressants volatile below 300°F was unsuccessful; morpholine, acetic acid, N-propylamine, and alcohols all gelled the silicate solution. A monomolecular layer of a wetting agent, Ultrawet, on the primer permitted excellent wetting but acted as a parting agent on heat-curing. Some polymers were prepared with asbestos fibers to make them more receptive to the ceramic formulations. Wettability was only slightly improved, however. A definite deficiency of this technique was the difficulty encountered in achieving a desirable paint texture.

A common difficulty encountered with combination coatings was the tendency for the ceramic to craze on curing, a fault less pronounced in phosphate compositions than in silicate. Crazeing was probably due to non-uniform shrinkage resulting from incomplete wetting.

Composite coatings with an organic as a protective strippable topcoat was an attractive possibility. The polymer investigated was an SP 500-pigmented LTV-602 silicone elastomer which would leave a relatively stable residue, if any, when removed. The porous nature of the inorganic silicate coating, however, permitted wedding of the two layers, and the coating was no longer strippable. Permeation was reduced slightly by brushing or trowelling the elastomer rather than by spraying.

E. Anomalous Degradation

An experiment was designed to determine the nature of the anomalous failure of the otherwise stable LTV-602-based paints when applied over a rutile-pigmented topcoat. This anomaly is described pictorially in Figure 62.

The dual-coat system was prepared in an attempt to utilize the reflective characteristics of high-refractive-index rutile titanium dioxide pigment and subsequently to protect it with a layer of stable zinc oxide-pigmented methyl silicone resin. The rutile paint, S-14, is based on 806A phenyl-methyl silicone resin and was formulated at a PVC of 30%. The LTV-602 paint, S-13, is pigmented with zinc oxide, also at a PVC of 30%.

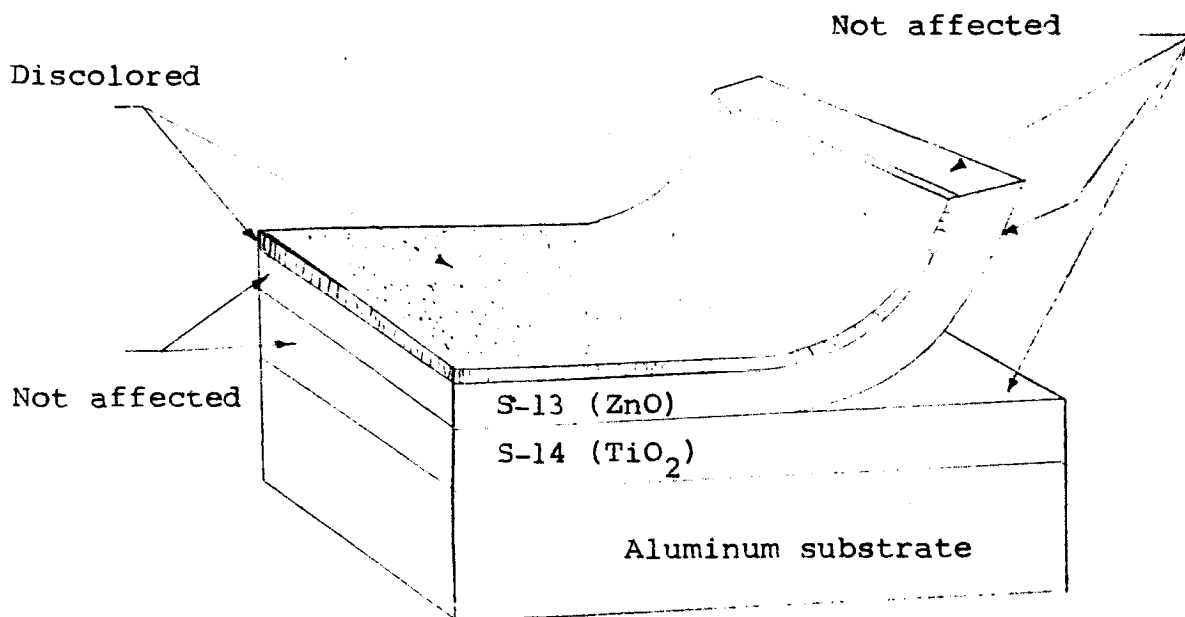


Figure 62

ANOMALOUS FAILURE OF DUAL-COAT REFLECTIVE PAINT SYSTEM

All tests resulted in severe discoloration of only the top outermost layer of S-13. The elastomeric S-13 was peeled from the hard, glossy S-14 primer. Examination showed that neither the underside of S-13 nor the surface of S-14 were affected in any way by the irradiation. This result prompted the following experiment.

Three specimens were prepared as follows. Two panels were each painted with about 3 mils of a rutile paint designated S-17 (45% PVC). One panel was painted with S-13. One of the two rutile paints was then given a 3-mil topcoat of S-13. The rutile substrate had been baked for 1 hour at 500°F.

Figure 63 shows the anomalous degradation which occurred when the "stable elastomeric" coating was used over the unstable rutile paint. Subsequent tests showed that a stable resin-based zinc oxide paint (S-20) also degraded more severely when used as a topcoat over S-14, the rutile paint pigmented at 30% PVC. This phenomenon cannot be explained in terms of our experience with these materials:

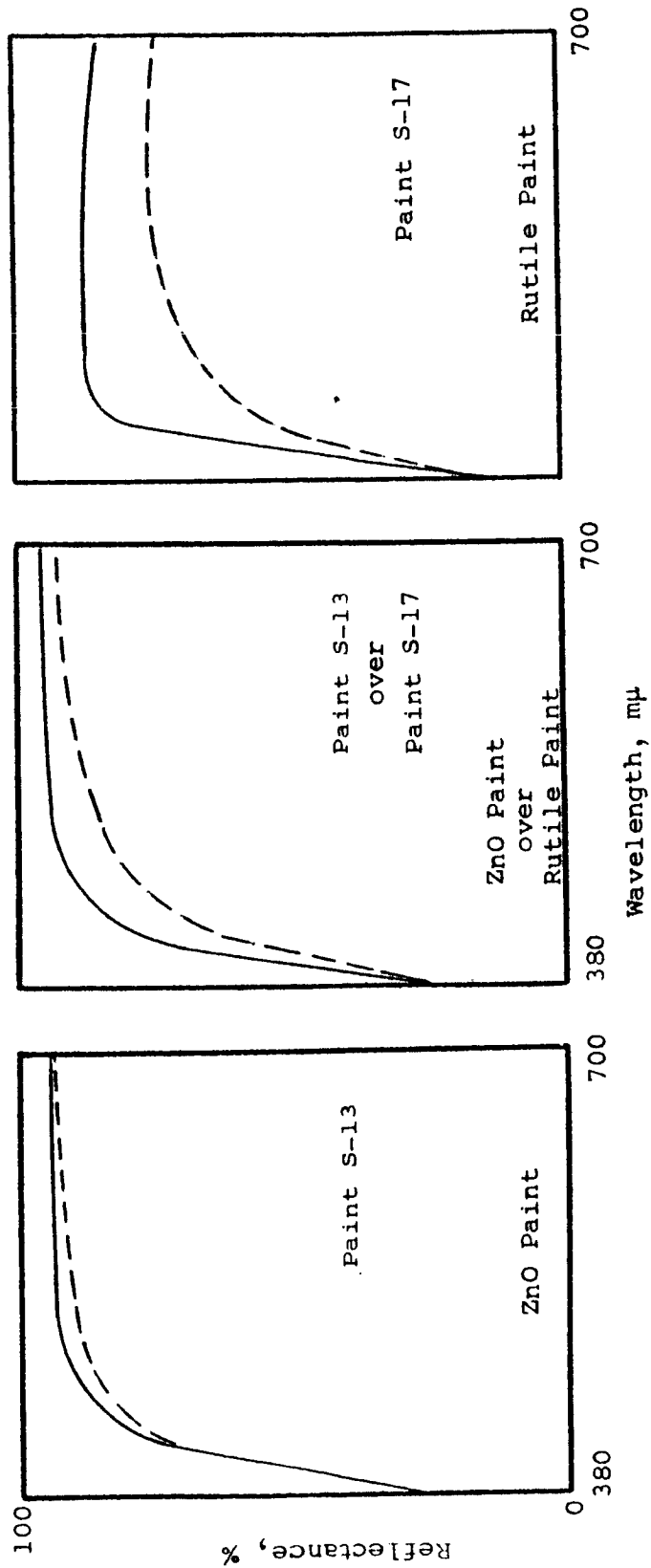


Figure 63
ANOMALOUS DEGRADATION OF A DUAL-COAT REFLECTIVE PAINT SYSTEM
UPON UV IRRADIATION FOR 500 ESH IN VACUUM

F. Attenuated Total Reflectance

This new and potentially very useful technique is based on the variation of the refractive index in the region of an absorption band. It is well known that total internal reflectance occurs when a beam of light crosses an interface at an angle greater than the critical angle. This angle is determined by the ratio of the refractive indices of the phases which form the interface, and total internal reflection can only occur when radiation passes from a medium of high refractive index to one of lower refractive index. Therefore the critical angle varies with the refractive index of the second phase, if the refractive index of the first phase remains constant. Since the refractive index of a substance is anomalous in the region of an absorption band, it is to be expected that the reflectance of light near the critical angle will be a function of the absorption spectrum of the second phase.

Since attenuated total reflectance is an interfacial phenomenon, it is sensitive only to the surface composition of the second phase. This is a particular advantage in the study of photolysis of solid materials, since the reaction has been shown to be confined to the surface of the material. Even if the coatings of interest to this project were transparent to infrared radiation (which they cannot be because of the requirements of high emittance), a conventional transmission study of the changes produced by the photolysis would be relatively insensitive to changes produced on the surface, since conventional transmission techniques characterize the bulk of the material.

In principle, then, this technique seems uniquely suitable for this investigation. In practice, however, there are practical difficulties, the greatest of which is obtaining true optical contact between the high refractive index prism (Figure 64) and the specimen. Various devices have been suggested such as a film of Nujol or some other transparent liquid, but thus far none have given the necessary degree of reproducibility.

In order to detect small differences in samples before and after photolysis, the possibility of artifacts must be carefully excluded. Many coatings of interest to this project are highly pigmented and therefore do not have optically smooth surfaces. Some are even sufficiently porous that excessive amounts of Nujol are required to exclude air from the interface, and the spectrum thereby loses definition. At present, the best procedure involves the use of a silver chloride prism, which is clamped against the specimen for 8 hours before the spectrum is obtained. Since silver chloride is relatively soft, it deforms under continued pressure, and eventually a reproducible

spectrum is obtained. These spectra, however, have not been of sufficient quality to show, for example, changes in functional group concentration produced by photolysis.

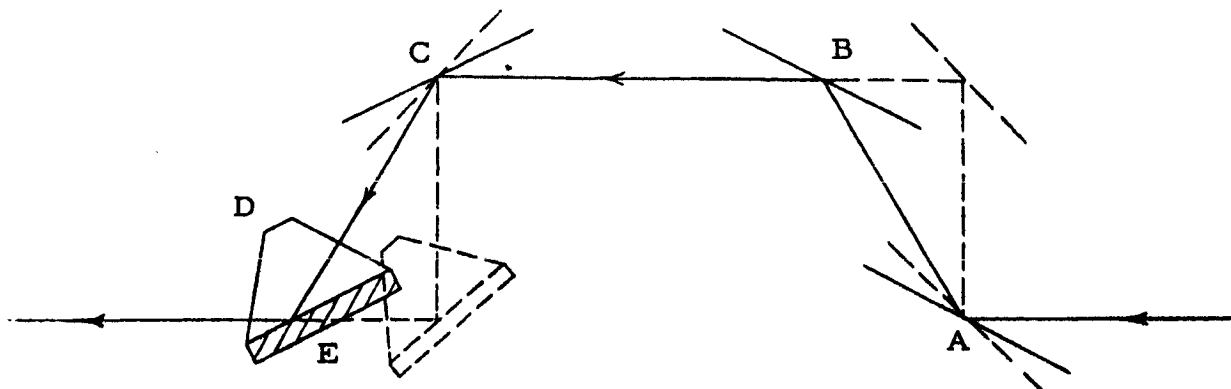


Figure 64

ATTENUATED TOTAL REFLECTANCE

The source of difficulty is clearly in the nature of the specimens. When a polymer solution is applied directly to the prism and an adhering film is formed by evaporation, excellent characteristic spectra are obtained. Figure 65 shows such a film and the effect of varying the angle of incidence. The spectrum is scarcely sensitive to the angle of incidence once the critical angle is exceeded, but below this angle the spectrum is predictably poor.

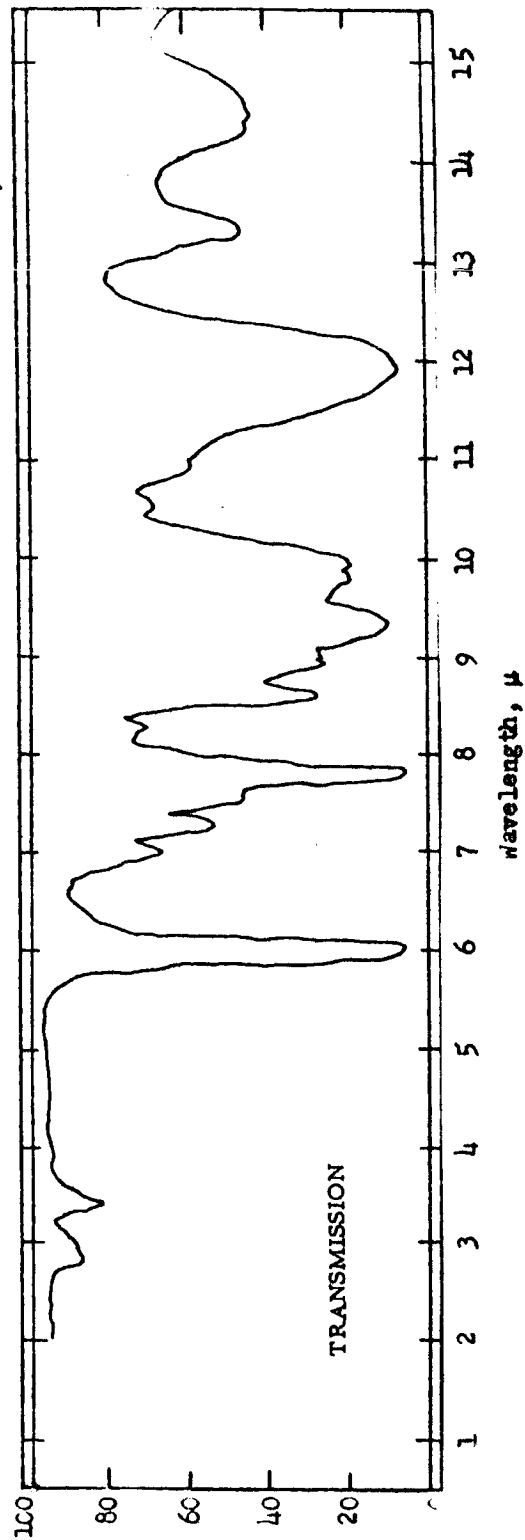
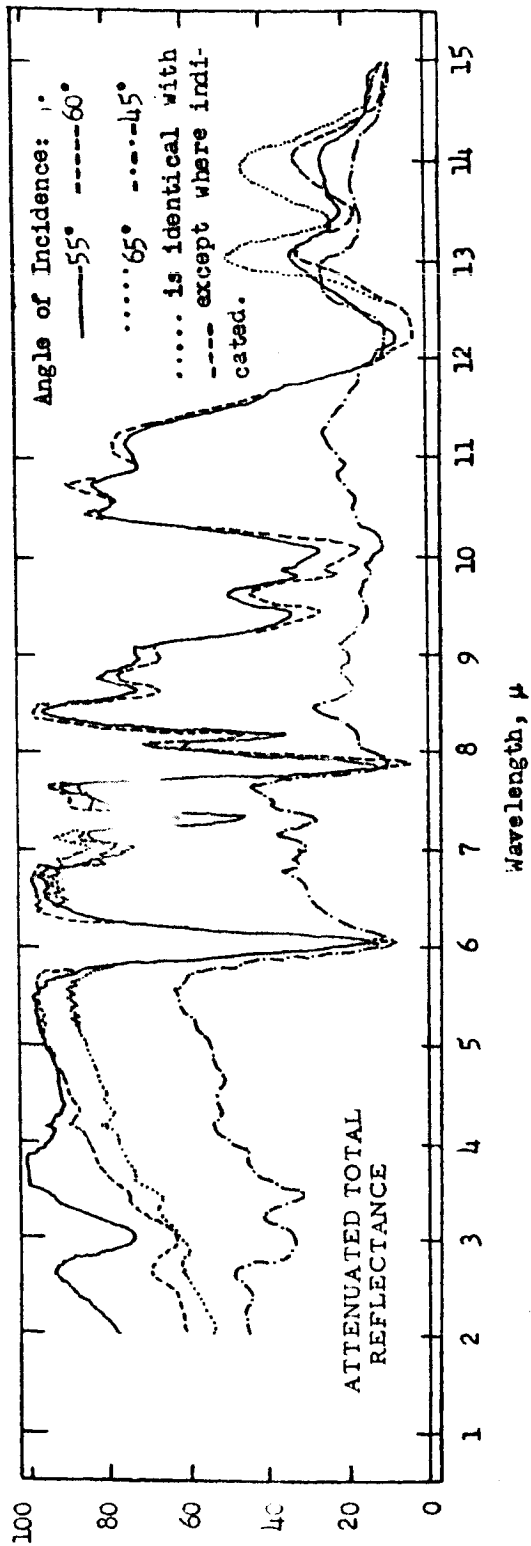


Figure 65
 COMPARISON OF ATTENUATED TOTAL REFLECTANCE AND TRANSMISSION SPECTRA

XI. CONCLUSIONS

1. Of the pigments studied, zinc oxide, zinc sulfide, and calcined china clay were the most satisfactory, in that order.

2. Of the vehicles studied, alkali silicates and methyl silicones were the most satisfactory.

3. The desired properties for a spacecraft-thermal-control coating were obtained through the use of a high-purity zinc oxide, SP 500, in conjunction with either a methyl silicone polymer synthesized in our laboratories or a commercial potassium silicate, PS7.

4. The solar absorptance of both systems changed less than 0.02 after exposure to over 4000 equivalent sun-hours of ultraviolet irradiation in vacuum.

63-552

APPENDIX I - COATING AND RESIN NUMBERS

INORGANIC COATINGS

| <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> | <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> |
|------------------------------------|---|------------------------------------|---|
| C1 | 2-5-3 | C44 | 1-9-2 |
| C2 | 2-13-5 | C45 | 1-16-6 |
| C3 | 2-4-3 | C46 | 1-19-2 |
| C4 | 2-5-4 | C47 | AM |
| C5 | 2-24-2 | C48 | HS |
| C6 | 3-5-0 | C49 | NH ₃ |
| C7 | 3-15-4 | C50 | 1-23-0 |
| C8 | 1-12-4 | C51 | 1-25-0 |
| C9 | 2-12-0 | C52 | 2-11-3 |
| C10 | 2-11-0 | C53 | 2-11-4 |
| C11 | 2-20-5 | C54 | 2-12-4 |
| C12 | 2-20-6 | C55 | 3-21-6 |
| C13 | 2-20-4 | C56 | 1-9-4 |
| C14 | 2-24-4 | C57 | 2-13-3 |
| C15 | 2-24-5 | | |
| C16 | 3-2-3c | | |
| C17 | 2-20-4a | | |
| C18 | 2-10-0 | | |
| C19 | 2-23-3 | | |
| C20 | 2-25-2c | | |
| C21 | 3-4-5a | | |
| C22 | 2-10-3 | | |
| C23 | 2-17-3 | | |
| C24 | 2-17-3 HC | | |
| C25 | 2-17-8 | | |
| C26 | 2-18-2 | | |
| C27 | 2-18-4 | | |
| C28 | 2-19-0 | | |
| C29 | 2-19-1 | | |
| C30 | 2-20-0 | | |
| C31 | 2-9-4 | | |
| C32 | 2-10-5 | | |
| C33 | 2-10-6 | | |
| C34 | 2-18-3 | | |
| C35 | 2-18-5 | | |
| C36 | 2-20-2 | | |
| C37 | 2-25-3 | | |
| C38 | 2-25-4 | | |
| C39 | 2-24-0 | | |
| C40 | 2-24-6 | | |
| C41 | 2-24-7 | | |
| C42 | 2-24-0a | | |
| C43 | 1-5-4 | | |

INORGANIC COATINGS

| <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> | <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> |
|------------------------------------|---|------------------------------------|---|
| Z1 | 1-9-5 | Z49 | 3-19-6f |
| Z2 | 2-13-0b | Z50 | 4-16-2c |
| Z3 | 2-12-3b | Z51 | 3-24-6b |
| Z4 | 2-10-7 | Z52 | 441-2b |
| Z5 | 2-13-0a | Z53 | 441-2a |
| Z6 | 2-13-01 | Z54 | 5-14-6 |
| Z7 | 2-9-0 | Z55 | 3-24-4a |
| Z8 | 2-12-3a | Z56 | 4-11-4a |
| Z9 | 2-10-7a | Z57 | 3-24-5b |
| Z10 | 2-16-3x | Z58 | 3-21-5gB |
| Z11 | 2-17-2a | Z59 | 3-19-6a2 |
| Z12 | 2-17-2c | Z60 | W1 |
| Z13 | 2-18-0 | Z61 | WD |
| Z14 | 2-18-1 | Z62 | 4-15-2e |
| Z15 | 2-19-6 | Z63 | 4-18-24 |
| Z16 | 2-17-6 | Z64 | 4-16-0e |
| Z17 | 55 LO | Z65 | 4-16-0a |
| Z18 | 2-17-7 | Z66 | 441-1aA |
| Z19 | 2-22-7 | Z67 | 5-4-4J |
| Z20 | 2-24-1 | Z68 | 5-9-04 |
| Z21 | 2-23-0 | Z69 | 4-15-7f |
| Z22 | PS 7 | Z70 | 4-15-7e |
| Z23 | 3-24-7a | Z71 | 4-23-0a |
| Z24 | SP 30 | Z72 | 4-23-0b |
| Z25 | AZO 33 | Z73 | 4-20-31a |
| Z26 | XX 30 | Z74 | 4-20-31b |
| Z27 | 3-10-3a3 | Z75 | 4-23-71a |
| Z28 | 3-14-4c | Z76 | 4-23-71b |
| Z29 | 3-14-0f | Z77 | 4-15-2W |
| Z30 | 3-12-1b | Z78 | 4-16-0gl |
| Z31 | 3-13-6c | Z79 | 4-14-3e1 |
| Z32 | 3-12-46 | Z80 | 4-14-3e2 |
| Z33 | 3-14-2b | Z81 | 4-14-3e3 |
| Z34 | 3-13-5c | Z82 | 5-13-06 |
| Z35 | 3-10-6a | Z83 | 5-16-7 |
| Z36 | 3-12-2a | Z84 | 5-6-9 |
| Z37 | 3-14-1c | Z85 | 5-13-47 |
| Z38 | 3-14-3b | Z86 | 5-11-31 |
| Z39 | 3-15-02 | Z87 | 5-19-2 |
| Z40 | 3-15-1a | Z88 | 5-19-13 |
| Z41 | 3-15-2d | Z89 | 5-19-15 |
| Z42 | 3-15-3c | Z90 | 5-19-18 |
| Z43 | 3-19-6 | Z91 | 5-19-19 |
| Z44 | 3-13-5c | Z92 | 5-19-20 |
| Z45 | 3-10-1b4 | Z93 | 5-19-5 |
| Z46 | 3-14-2e | Z94 | 5-24-1 |
| Z47 | 3-14-0g | Z95 | 5-19-4 |
| Z48 | 441-1b | Z96 | 5-19-1 |

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ORGANIC COMPOUNDS

| <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> |
|------------------------------------|---|
|------------------------------------|---|

| | |
|------|----------------|
| P-1 | 413-2 |
| P-2 | 199 |
| P-3 | 193 |
| P-4 | 198 |
| P-5 | 30 |
| P-6 | 34 |
| P-7 | 169 |
| P-8 | 121 |
| P-9 | 176 |
| P-10 | 190 |
| P-11 | 118 |
| P-12 | 160 |
| P-13 | 185 |
| P-14 | 195 |
| P-15 | 157 |
| P-16 | 164 |
| P-17 | 154 |
| P-18 | 403-1 |
| P-19 | 416-1 |
| P-20 | 407-2 |
| P-21 | 409-2B |
| P-22 | 410-1a |
| S-1 | TC-83-5 |
| S-2 | TC-83-7 |
| S-3 | TC-83-8 |
| S-4 | TC-83-11 |
| S-5 | TC-83-12 |
| S-6 | TC-83-13 |
| S-7 | TC-83-16 |
| S-8 | TC-83-18 |
| S-9 | TC-83-19 |
| S-10 | TC-83-21 |
| S-11 | TC-50-8 |
| S-12 | TC-50-10 |
| S-13 | TC-50-11 |
| S-14 | P-50-15 |
| S-15 | TC-50-16 |
| S-16 | TC-50-17 |
| S-17 | TC-50-19 |
| S-18 | TC-50-22 |
| S-19 | TC-50-23 |
| S-20 | TC-50-24 |
| S-21 | TC-50-25 |
| S-22 | TC-46-2 |
| S-23 | TC-46-4 (TBT) |
| S-24 | TC-46-4 (Z775) |
| S-25 | TC-46-5 |

| <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> |
|------------------------------------|---|
|------------------------------------|---|

| | |
|------|----------|
| S-26 | TC-46-6 |
| S-27 | TC-46-8 |
| S-28 | P-46-9 |
| S-29 | TC-46-13 |
| S-30 | TC-46-14 |
| S-31 | TC-46-16 |
| S-32 | TC-46-19 |
| S-33 | TC-46-20 |

EXPERIMENTAL RESINS

| <u>No. Used in This Report</u> | <u>No. Used in Previous Reports</u> |
|------------------------------------|---|
| R-1 | S-83-10 |
| R-2 | S-83-14 |
| R-3 | S-83-17 |
| R-4 | S-83-20 |
| R-5 | S-50-3 |
| R-6 | S-50-4 |
| R-7 | S-50-12 |
| R-5A | S-50-3a1 |
| R-5B | S-50-3a2 |
| R-8 | VS-38-2a |
| R-9 | S-38-3 |

APPENDIX II - SPECIFICATIONS OF THE THREE BEST COATINGS

The following specifications are presented for the three best spacecraft-thermal-control coatings developed. These coatings are Z93, a zinc oxide-pigmented potassium silicate paint; S-13, a zinc oxide-pigmented methyl silicone elastomeric coating; and S-33, a zinc oxide-pigmented experimental methyl silicone resin paint. S-13 and S-33 were designated TC-50-11 and TC-46-20, respectively, in previous reports on this program.

PAINT Z93

Materials. SP 500 ZnO was obtained from New Jersey Zinc Co. The vehicle, PS7 potassium silicate, was obtained from Sylvania Electric Products Corp. The pigment is calcined at 700°C for 16 hr (heating and cooling rates are not critical).

Formulation. The materials are mixed in a pigment-to-binder weight ratio (PBR) of 4.30 and a solids content of 56.9%. A typical batch is 100 g ZnO, 50 cc PS7 (35% soln.), and 50 cc distilled water. Ball-milling of the ingredients is conducted with porcelain balls in a dense alumina mill. The volume ratio of balls to materials is 1:3, and the total charge is <50%. A milling time of 6 hr at 70% critical speed ($\text{rpm} = 54.2/\sqrt{\text{mill radius (ft)}}$) yields a satisfactory consistency for spraying and is recommended.

The paint is prepared just before it is to be used. Shelf life for this composition is limited. Actual shelf time should not exceed 24 hr, and the mixture should be shaken occasionally to resuspend the pigment.

Application. The formulation is applied by spray-painting. The gas pressure should be clean; prepurified nitrogen is a good source. Aluminum or plastic substrates should be abraded, e.g., with #60 Aloxite metal cloth, and thoroughly washed with detergent and water.

The application technique consists of spraying at a distance of 6 to 12 in. until a reflection due to the liquid is apparent. This is followed by air-drying until the gloss is practically gone, at which time the spraying-drying cycle is repeated. A thickness of about 1 mil is achieved per cycle. Coating dimensions can therefore be predictably applied. However, hand-spraying is inherently an art and not a science, and experience must be gained by the individual painter to determine the most satisfactory technique for him.

Reapplication. The porous nature of a cured coating necessitates heavy spraying upon application of a second coat, which yields the characteristic gloss of a satisfactory, finished texture. If the area to be repainted has been contaminated, it should be scrupulously cleaned with detergent and water. If desired, the paint can be removed simply by abrasion, since it is somewhat soft.

Curing. Satisfactory physical properties are obtained by an air-drying cure. Improved hardness is obtained by heat-curing at 140°C. Strict adherence to cleanliness

should be observed during this step as in all the other steps. The presence of impurities can greatly decrease the stability of paints to the space environment.

Physical Properties. The coating is porous and relatively soft. It exhibits good resistance to thermal-shock treatment consisting of immersion in liquid nitrogen followed by heating to 200°F. The departure of Z93 from the usual brittle nature of ceramics enables it to withstand stresses well. Soiling tendencies, however, are high. Cleaning can be accomplished with detergent and water. Acetone and similar organic solvents must be avoided since they leave a degradable residue.

Optical Properties Minimal solar absorptance (α) is approached at a coating thickness of 4 mils, where the predicted α is 0.16 ± 0.01 . A thickness of 5 mils yields a minimum α of 0.15. For satisfactory physical properties, coatings of 6 mils or less are desirable. The working range therefore should be between 4 and 6 mils. Emittance (ϵ) is relatively insensitive to coating thickness, and values >0.90 can be expected at 2 mils or greater.

Stability to UV Irradiation in Vacuum. The severest space-simulation test to which this material was subjected was for 4200 ESH; α increased 0.014. An identical composition which had been heated at 500°C for 2 hr before space simulation showed a gain in α of 0.007. Thus, good stability can be expected from Z93 if it is properly prepared

The importance of cleanliness in all aspects of handling cannot be overemphasized. The undesirable contribution to coloration by various contaminants was clearly demonstrated in several experiments

PAINT S-13

Materials The ingredients are New Jersey Zinc SP 500 ZnO, 240 parts by wt., General Electric LTV-602 silicone compound, 100 parts by wt., General Electric SRC-05 catalyst, 1 part by wt., and toluene, 183 parts by wt. The PVC is 30%, and the solids content is 40% by vol.

Formulation The ZnO, the LTV-602, and one-half the toluene are premixed and charged to a porcelain ball mill in a quantity sufficient to just fill the void space when the mill is half full of grinding stones. The paint is ground for about 16 hr at approximately 70% critical speed. The basic charge is then removed, and the remainder of the toluene is added to the mill. The residue and the solvent are ground until the contents are uniformly thin, but not for more than 5 min. The contents are then added to the main charge and the whole mixed thoroughly. NOTE: THE SRC-05 CATALYST IS NOT ADDED UNTIL THE PAINT IS APPLIED. Borundum-fortified porcelain mills and grinding media are recommended. Cleanliness of the ball mill is vital. Excellent shelf life was observed.

Application A primer is required and can be applied to any surface to which the specified primer will adhere. Either General Electric's proprietary SS-4004 or SS-4044 primer can be used. SS-4004 contains a red dye to facilitate control of thickness during application. Less than 1 mil of primer is required. The use of SS-4004 rather than SS-4044 results in a slightly higher (between 0.01 and 0.02) solar absorptance (α). The primer should be allowed to air-dry for 1 hr before the paint is applied.

Both S-13 and the primer are applied by spray-painting. A gas pressure of 30 to 35 psi is required when a Paasche type AUTF airbrush is used. The use of a larger gun may require experimentation with the gas pressure as well as with the solvent concentration. The gas pressure should be clean; prepurified nitrogen is recommended. The SRC-05 catalyst is added immediately before application, to an amount of paint no larger than that which can be applied in 20 to 30 min. The paint air-cures in 16 hr. Curing can be slightly accelerated by heating to 150 to 200°F.

Reapplication Soiled or damaged areas can be recoated. Soiled areas must be cleaned thoroughly with detergent and water. The surface must be dry before application of additional S-13. Damaged or gouged areas can be recoated by making a paste of S-13 in which the bulk of the solvent is omitted. Such a material can be trowelled or brushed over the damaged area and cures tack-free in a few hours.

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Physical Properties. Paint S-13 is rubbery and resilient. Therefore, it can be gouged by a sharp tool with little effort. Its adherence is excellent when a primer is used but is very poor when applied directly to a metal substrate, in which case it can be stripped from the substrate in one piece. Because of the resiliency of the surface, dirt tends to cling to the surface. Dirt can be easily removed by wiping with a water-moistened CLEAN, SOFT cloth. NOTE: S-13 SHOULD NEVER BE CLEANED WITH ORGANIC SOLVENT (EXCEPT AT A SACRIFICE TO STABILITY). Paint S-13 withstands more than 10 thermal-shock cycles consisting of immersion in liquid nitrogen followed by rapid heating to 200°F. The paint can be torsionally stressed to 90° without failure and withstands repeated bending to 180°.

Optical Properties. Minimal α is not obtained until a thickness of nearly 10 mils is reached. The following tabulation is provided as a guide.

| Thickness (± 0.25 mils) | Solar Absorptance (± 0.01) |
|---------------------------------|-------------------------------------|
| 1 | 0.33 |
| 2 | .27 |
| 3 | .25 |
| 4 | .23 |
| 5 | .22 |
| 6 | .21 |
| 8 | .20 |
| 9 | .19 |
| 10 | 0.19 |

A working range of 5 to 8 mils is recommended. For coatings of 4 mils or thicker, the total normal emittance (200°F) is 0.90 or better.

Stability to UV Irradiation in Vacuum. The severest test to which this material was subjected was for 4200 ESH; α increased from 0.21 to 0.25, with $\Delta\alpha = 0.06$. Cleaning with water or with detergent and water before irradiation does not affect stability. Cleaning with acetone, however, severely affects stability. Therefore cleaning with water or with water and detergent is recommended.

PAINT S-33

Materials. This paint is based on an experimental methyl silicone resin synthesized at the IIT Research Institute. The pigment is New Jersey Zinc SP 500 ZnO. Tetrabutoxy titanium (TBT) is used as a cross-linking (curing) agent and can be obtained from Du Pont.

The experimental resin, R-9, is prepared as follows. Three-tenths moles (38.7 g) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 g) of methyltrichlorosilane (95%) are mixed in 300 g of anhydrous diethyl ether. The resultant mixture is added dropwise with agitation, over a period of 40 min, to 1000 g of ice. The ether layer is separated and washed with a 5% soln. of sodium bicarbonate, followed by three washings with distilled water. The ether soln. is dried over Drierite and evaporated at reduced pressure, leaving a viscous colorless resin. This stock resin is distilled at 100 to 107°C at a pressure of 0.01 to 0.04 mm Hg in an ASCO 50 Rota-Film molecular still. The upper-molecular-weight fraction is collected as resin R-9. It should possess a molecular weight of 2000 to 2200, the lower limit being critical. The resin is decolorized with Darco Activated Carbon G60 obtained from the Atlas Powder Co.

The ingredients of the paint are New Jersey Zinc SP 500 ZnO, 316 parts by wt., IITRI experimental silicone resin R-9, 100 parts by wt., tetrabutoxy titanium (TBT), 1 part by wt., and toluene, 225 parts by wt. The PVC is 40%, and the solids content is 40% by vol.

Formulation. The ZnO, the R-9 resin, and 100 parts of the specified toluene are premixed and charged to a porcelain ball mill in a quantity sufficient to just fill the void space when the mill is half full of grinding stones. Borundum-fortified porcelain mills and grinding media are recommended. Excellent shelf life was observed. The paint is ground for about 16 hr at approximately 70% critical speed. The TBT is added just prior to application. The basic charge is removed and 100 parts of the toluene are added to the mill. The residue and solvent are ground until the contents are uniformly thin, but not for more than 5 min. The contents are then added to the main charge and the whole mixed thoroughly. The TBT and the remaining 25 parts of the toluene are mixed together and slowly added to the paint, with agitation. Local gelation can be broken down by vigorous agitation or stirring. Excellent shelf life was observed.

This formulation is semiglossy when cured. A glossy paint can be made by cutting the amount of pigment required to 264 parts by wt. and the toluene to 176 parts by wt. The PVC is 35%.

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Application Paint S-33 does not require a primer. The surface to which it is applied must be absolutely dry and should be lightly sandblasted, pressure-blasted, or abraded with, e.g., #60 Aloxite metal cloth. Adherence to aluminum, magnesium, and steel substrates is excellent if these surfaces are clean. Its adherence to other surfaces is unknown.

S-33 is best applied by spray-painting at a gas pressure of 30 to 35 psi when a Paasche type AUTF airbrush is used. The use of a larger gun may require experimentation with gas pressure as well as with the solvent concentration. The gas pressure should be clean; prepurified nitrogen is recommended. The paint should be allowed to air-dry for 1 to 2 hr, or until the solvent has evaporated. It should then be heat-cured for 1 to 2 hr at 300°F. Postcuring for 1 hr at 500°F results in a harder, more brittle, less glossy film which exhibits still greater stability to UV vacuum exposure.

Physical Properties Paint S-33 is hard and brittle. It resists soiling, particularly when pigmented at 35% rather than 40% PVC. It does not remain intact when bent 90° around a 1/2-in. mandrel, but withstands torsional stress to 90°. It withstands 10 cycles of thermal-shock treatment consisting of immersion in liquid nitrogen followed by rapid heating to 200°F. Cleaning can be accomplished by washing with a detergent followed by copious quantities of distilled water. The effect of cleaning with organic solvents is unknown, and therefore organic solvents are not recommended.

Optical Properties Minimal solar absorptance (α) is reached at a thickness of approximately 7 mils. The following tabulation is provided as a guide.

| Thickness (± 0.25 mils) | Solar Absorptance (± 0.01) | Total Normal Emittance (200°F) |
|---------------------------------|-------------------------------------|-----------------------------------|
| 1 | 0.29 | 0.80 |
| 2 | .25 | .88 |
| 3 | .23 | .89 |
| 5 | .205 | .90 |
| 6 | .20 | .91 |
| 7 | 0.195 | 0.92 |

A working range of 3 to 5 mils is recommended. The emittances provided above are estimates based on data which showed considerable scatter.

Stability to UV Irradiation in Vacuum The severest test to which paint S-33 was subjected was for 4200 ESH. A specimen of S-33 which was cured for 1 hr at 300°F increased 0.020 in α , whereas a specimen postcured for 1 hr at 500°F increased 0.011. The paint, if pigmented at only 35% PVC, is somewhat less stable, and α may increase 0.02 upon 2000-ESH exposure.

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